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Cover Photo: Shoepack Lake, Minnesota, Summer 1985. This lake is included in the Long-Term Monitoring Project. Photo by Kathy Webster, Wisconsin Department of Natural Resources, Woodruff, Wisconsin.

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16. ABSTRACT

The Long-Term Monitoring Project was originally designed to monitor trends in low ANC surface waters across a gradient of acidic atmospheric deposition. Only lake data are presented in this report. A total of 121 lakes in four regions of the U.S. were sampled. Historical data were available for some subregions, resulting in a 7-year record of seasonal samples. Due to this short period of record and to the inconsistent sampling schedules of the historical data, trend analysis was not performed on the Long-Term Monitoring Project data; however, the data were useful for examination of design aspects for a monitoring program. These data were used to estimate the number of lakes that should be sampled in the subregions studied and the number of samples that should be taken through time in a single lake in order to detect a given level of change with specified confidence. Spring and fall chemistry were compared across subregions in order to determine the relationship between seasons and the usefulness of a fall index sample. Fall chemistry had a strong relationship to spring chemistry, which differed among subregions and among years. These results are presented and discussed thus providing guidelines for the design of future monitoring programs.

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FOREWORD

As part of the National Acid Precipitation Assessment Program (NAPAP), a Federal Interagency Task Force mandated by Congress in 1980, the U.S. Environmental Protection Agency (EPA) in 1982 initiated a program of long-term lake and stream monitoring (LTM). Organized in concert with the other member agencies of the NAPAP Aquatic Effects Task Group, this monitoring program preceded the National Surface Water Survey (NSWS) and the organization of the EPA Aquatic Effects Research Program (AERP).

The goals of the LTM program were to detect and measure deposition related trends in the chemistry of low acid neutralizing capacity (ANC) surface waters, and to compare the response of these waters over geographic gradients of sulfate and hydrogen ion deposition as well as among different major geographic regions receiving comparable deposition.

The initiation of the NSWS in 1984 introduced new approaches to the regional assessment of the aquatic effects of acidic deposition. The national lake and stream surveys obtained regionally representative probability samples from well-defined populations of lakes and streams, which would allow a reselection of monitoring sites that would better enable characterization of trends across regions. Such a selection was not possible when the original LTM sites were defined. Consequently, planning is now underway for a new monitoring project, the Temporal Integrated Monitoring of Ecosystems (TIME), that will replace and subsume the present monitoring effort. The TIME project has the following objectives:

1. Provide the earliest indication of regional trends in surface water acidification or recovery.
2. Quantify, with known certainty, the rate at which acidification or recovery is occurring, the subpopulation characteristics of the affected lakes or streams, and the subregional extent of these systems.
3. Correlate trends in regional atmospheric deposition with regional trends in surface water chemistry.
4. Correlate changes in water chemistry with biological changes in order to develop indices for assessing regional effects of chemical changes on aquatic biota.

This new project is being developed with the input and assistance of existing LTM cooperators, and is expected to include at least some of the presently monitored lakes and streams. TIME is scheduled to begin in the spring of 1989.

ABSTRACT

The Long-Term Monitoring Project was originally designed to monitor trends in low ANC surface waters across a gradient of acidic atmospheric deposition. Monitoring of both streams and lakes was funded by the project; however, only lake data are presented in this report. A total of 121 lakes in 4 regions of the United States were sampled. Historical data were available for some subregions, resulting in, at most, a 7-year record of seasonal samples. Due to this short period of record and to the inconsistent sampling schedules of the historical data, trend analysis was not performed on the Long-Term Monitoring Project data; however, the data were useful for examination of design aspects for a monitoring program. Long-Term Monitoring Project data were used to estimate the number of lakes that should be sampled in the subregions studied and the number of samples that should be taken through time in a single lake in order to detect a given level of change with specified confidence. Spring and fall chemistry were compared across subregions in order to determine the relationship between seasons and the usefulness of a fall index sample. Fall chemistry had a strong relationship to spring chemistry, which differed among subregions and among years. These results are presented and discussed, thus providing guidelines for the design of future monitoring programs.

SUMMARY

The following conclusions have been drawn from the data analysis of the current Long-Term Monitoring (LTM) Program:

1. The LTM lakes were low acid neutralizing capacity (ANC) systems, whose values generally are lower than the National Lake Survey (NLS) median values. In keeping with the low ANC values, LTM lakes were also generally low in pH and Ca compared to lakes in the NLS. Dissolved organic carbon (DOC) values were low in LTM systems in the Upper Midwest and in Maine. Physical characteristics of the LTM lakes corresponded well with the NLS populations, except in the Southern Blue Ridge, where 4 of the 12 LTM lakes were larger than 2000 hectares (ha). LTM lakes were generally well distributed across the range of chemical parameters.

2. Visual inspection of chemical data plotted over time revealed no obvious trends in the data. Rates of change due to acidic deposition in aquatic systems are expected to be slow, thus detectable changes are not expected to occur in a 2- to 7-year time span. For these reasons, no trend analyses were performed.

3. Quality assurance (QA) data were too sparse to adequately describe the quality of the data. Increasing the number of duplicate and replicate samples will improve QA efforts in the future. Audit sample analyses were too variable to describe the accuracy of LTM data. Comparison of these data with other laboratory analyses and with internally prepared samples indicated that synthetic audit samples were not stable enough to assess laboratory accuracy.

4. Increasing the numbers of lakes sampled in each region would allow smaller changes in lake chemistry to be detected with increased confidence and power. Estimates of the numbers of lakes that should be sampled in each region for three levels of change and several levels of significance and power are included in Appendix D.

5. Data from the LTM Program were also used to estimate the duration of monitoring that would be required for the detection of differing levels of change with specified confidence. These data generally indicate that in most regions, monitoring must continue for longer than 7 years to enable the detection of within-lake trends.

6. Variability analyses demonstrated that among-lake variability exceeded annual and seasonal variability, indicating that sampling more lakes in a region would allow a more accurate characterization of regional trends than would sampling a similar number of lakes more intensively.

7. Analyses that include precipitation and temperature data indicate that meteorological data explain significant variation in some regions. Consideration of these data would facilitate accurate descriptions of trends in monitored lakes.

8. The influence of these results on the development of future monitoring projects is discussed in Section 4.2 of this report.

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ABBREVIATIONS AND SYMBOLS

ABBREVIATIONS

AAS -- atomic absorption spectrophotometry
AERP -- Aquatic Effects Research Program
ANC -- acid neutralizing capacity
DIC -- dissolved inorganic carbon
DOC -- dissolved organic carbon
ELS -- Eastern Lake Survey
EPA -- Environmental Protection Agency
EPRI -- Electric Power Research Institute
ERL-C -- Environmental Research Laboratory-Corvallis
FWS -- Fish and Wildlife Service
ICP -- Inductively coupled plasma emission spectrophotometry
LTM -- Long-Term Monitoring
ME -- Maine
MI -- Michigan
MN -- Minnesota
NADP -- National Acid Deposition Program
NAPAP -- National Acid Precipitation Assessment Program
NLS -- National Lake Survey, consisting of Eastern and Western Lake Surveys
NOAA -- National Oceanographic and Atmospheric Administration
NPS -- National Park Service
NSWS -- National Surface Water Survey
NY -- New York
PCA -- Principal Component Analysis
QA/QC -- quality assurance/quality control
RILWAS -- Regionalized Integrated Lake/Watershed Acidification Study
SBR -- Southern Blue Ridge
TG-E -- Aquatic Effects Task Group
TIME -- Temporal Integrated Monitoring of Ecosystems
TVA -- Tennessee Valley Authority
UPMW -- Upper Midwest
USDA-FS -- U.S. Department of Agriculture Forest Service
USEPA -- U.S. Environmental Protection Agency
USGS -- U.S. Geological Survey
VT -- Vermont
WI -- Wisconsin
WLS -- Western Lake Survey
1A -- Adirondack Region of NLS
1C -- Central New England Region of NLS; Vermont
1E -- Maine Region of NLS
2A -- Northeastern Minnesota Region of NLS
2B -- Upper Peninsula of Michigan Region of NLS

ABBREVIATIONS AND SYMBOLS (Continued)

2C -- Northcentral Wisconsin Region of NLS
2D -- Upper Great Lakes Region of NLS
3A -- Southern Blue Ridge Region of NLS (southern Appalachians)
4E -- Southern Rockies Region of NLS; Colorado

SYMBOLS

Al -- aluminum
Ca -- calcium
$Ca\ (HCO_3)_2$ -- calcium bicarbonate
$CaSO_4$ -- calcium sulfate
Cl^- -- chloride
$CO_3{}^{-2}$ -- carbonate
F^- -- fluoride
Fe -- iron
$F(x)$ -- cumulative frequency distribution
H^+ -- hydrogen ion
ha -- hectare
$HCO_3{}^-$ -- bicarbonate
IV -- indicator variable
K -- potassium
kg -- kilogram
$LnCl$ -- lanthanum chloride
m -- meters or slope of regression
Mg -- magnesium
Mn -- manganese
n -- number
Na -- sodium
$NaCl$ -- sodium chloride
$Na + K$ -- sodium and potassium
N_2O -- nitrous oxide
$NO_3{}^-$ -- nitrate
NH_4 -- ammonium
pH -- the negative logarithm of the hydrogen ion molar concentration; waters with lower pH are more acidic; a difference of one pH unit indicates a 10-fold difference in H^+ concentration
R^2 -- coefficient of multiple determination
$\hat{s}_e{}^2$ -- estimated variance
SiO_2 -- silicon quartz
$SO_4{}^{-2}$ -- sulfate
Z -- critical values of the standard normal distribution
$\mu eq\ L^{-1}$ -- microequivalents per liter
$\mu g\ L^{-1}$ -- micrograms per liter
α -- probability of rejecting the null hypotheses when it is true. $1-\alpha$ is commonly referred to as the significance level.

ABBREVIATIONS AND SYMBOLS (Continued)

β -- probability of failing to reject the null hypothesis when it is false. $1-\beta$ is commonly referred to as the power of a test.

Δ -- amount of change

θ -- first order lag correlation coefficient of the sample

CONTRIBUTORS

In addition to the authors of this report, the following people contributed to data management and data analysis.

Data Management: Les Hook and Richard Olson of Oak Ridge National Laboratory.

Data Analysis: Daniel Goodman and Mark Taper of Montana State University at Bozeman provided the principal component analysis.

James Blick and Mark DeHaan of Northrop Environmental Services created density contours on trilinear plots and provided advice on all data analysis.

Dave Thomas and Fred Ramsey, Department of Statistics at Oregon State University were consulted on the assessment of annual and seasonal variability, trends present in the data, calculations of regional sample size and duration of monitoring.

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SECTION 1

INTRODUCTION

1.1 LONG-TERM MONITORING PROGRAM BACKGROUND AND OBJECTIVES

1.1.1 Background

In 1982, the U.S. Environmental Protection Agency (USEPA) initiated a program for long-term chemical monitoring of surface waters under the National Acid Precipitation Assessment Program (NAPAP). In July 1982, the Aquatic Effects Task Group (TG-E) organized an ad hoc committee whose task was to develop the framework for a national program along with a standardized sampling and chemical analysis monitoring protocol to guide such a program. The committee included representatives from the following agencies, all of which are involved or interested in environmental monitoring:

- Environmental Protection Agency (EPA)
- Geological Survey (USGS)
- Tennessee Valley Authority (TVA)
- Fish and Wildlife Service (FWS)
- Forest Service (USDA-FS)
- National Park Service (NPS)

In January 1983, the committee produced a draft protocol that was used as a provisional guide for the EPA program. After extensive peer review, this document was revised and approved as the basis for the EPA program. The final version of this document appears in Appendix A. By 1985, EPA was supporting the monitoring of 121 lakes and reservoirs in 10 states (Table 1-1). Twenty-three streams in four regions were also chosen for monitoring. In cooperation with the USGS, stream monitoring was conducted in the Catskill Mountains in New York, the Laurel Ridge area of Pennsylvania, and the Sandhills section of the North Carolina Piedmont. USGS will publish reports on all three projects in 1987. Through the TVA, streams in the Southern Blue Ridge Province of North Carolina, Tennessee, and Georgia were monitored. The results have been reported to the EPA.

1.1.2 Objectives

The EPA Long Term Monitoring (LTM) Program was initially designed to detect and measure trends in the chemistry of low acid neutralizing capacity (ANC) surface waters over gradients of H^+ and SO_4^{-2} deposition and in different geographic regions receiving comparable deposition. These objectives cannot be addressed by this report because data have not yet been collected over a long enough period to determine if trends have occurred. However, a number of analyses are presented that relate to regional lake characteristics and can be used to assist in optimizing the planning for future programs.

The existing monitoring program, the results of which are treated in this report, was initiated before the National Surface Water Survey (NSWS) (Linthurst et al. 1986; Landers et al.

TABLE 1-1. EPA FUNDED LONG-TERM LAKE MONITORING PROJECTS

Location	Principal Investigator	Affiliation	Number of lakes	Start	Sampling Schedule	Comments
Adirondacks, New York	Charles Driscoll	Syracuse Univ.	17	Spring 1985	Monthly	Historical data, sampled monthly, from 1982-1984[1].
Vermont	Wallace McLean	Vermont Agency of Environmental Conservation	36	Winter 1981	Seasonal	Sampling and analytical changes (SO_4^{-2}) occurred in spring 1985.
Maine	Terry Haines	FWS; U. of Maine	6	Fall 1982	Spring, summer, fall	
Upper Midwest	Patrick Brezonik Katherine Webster	U. of Minnesota; Wisconsin Dept. of Natural Resources			Spring, summer, fall	Historical data, sampled sporadically on a seasonal basis, from 1978 to 1983[2].
Minnesota			11	Fall 1983		
Wisconsin			15	Fall 1983		
Michigan			14	Fall 1983		
Southern Blue Ridge Province of North Carolina, Tennessee, Georgia	Harvey Olem	TVA	12	Fall 1982	Spring, summer, fall	No samples taken in summer or fall 1983.
Rocky Mountains, Colorado	John Turk	USGS EPA Region VIII State of Colorado	10	Summer 1985	Monthly in summer	
TOTAL			121			

---

[1] Two years of additional data collected for most of these lakes between 1983 and 1985 by Syracuse University were funded by the Electric Power Research Institute during the Regional Integrated Lake Watershed Acidification Study.

[2] Data collected by the Univ. of Minnesota-Duluth and the Wisconsin Department of Natural Resources through a cooperative agreement with the Environmental Research Laboratory, Duluth, are available for most of these lakes for the period 1978-1982. The sampling schedule for these lakes was variable, ranging from twice a year to seasonally, and included multiple samples per lake.

1987; Messer et al. 1986) was carried out; thus regionally representative probability samples of defined populations of lakes were not available to assist in the selection of lakes. The LTM lakes chosen make up a sample with an unknown probability of selection from an undefined population. An estimation of regional trends requires the selection of a statistically rigorous probability sample from a well-defined population.

1.2 SITE SELECTION AND MONITORING

Lake monitoring sites were selected in areas where annual sulfate deposition was approximately 0-10, 10-20, and 20-30 kg/ha, with average volume-weighted precipitation pH ranging from about 5.5 to 4.3. In addition, sites were chosen to provide data from geographically separate regions, for example, New England and the Southern Appalachians, that receive comparable sulfate and hydrogen ion deposition. A listing of monitored lakes, together with location, elevation, lake type, and lake surface area appears in Appendix B. Table 1-2 summarizes information on the nearby National Acid Deposition Program (NADP) deposition collection sites.

Specific selection criteria included:

- ANC <200 μeq L^{-1}
- No recent land use changes or prospect of future changes
- Absence of local atmospheric pollutant sources
- Accessibility
- No recent history of forest fires or logging in the watershed
- No chemical manipulation of lake or watershed

Where possible, sites with good historical data that extended the period of record were given preference. The national and regional alkalinity maps generated by EPA (Omernik and Powers 1983; Omernik and Kinney 1985; Omernik and Griffith 1985) assisted in the identification of regions where surface waters with ANC less than 200 μeq L^{-1} were common.

Lakes were selected for monitoring in the following areas:

- The Adirondack Mountains in New York
- Vermont
- Maine
- The Upper Midwest lake district in Minnesota, Wisconsin, and Michigan
- The Southern Appalachians (TVA reservoirs in the Southern Blue Ridge Province of North Carolina, Tennessee, and Georgia)
- The Rocky Mountains

These locations not only provided a regional sampling of low ANC waters, but were distributed across hydrogen ion and sulfate deposition gradients (Table 1-2). A few higher ANC lakes in some areas were included to provide information on less susceptible systems. The following subsections provide some background information for each of the regions included in the LTM program.

TABLE 1-2. ANNUAL MEAN PRECIPITATION pH AND SULFATE IN WET DEPOSITION, AND PRECIPITATION QUANTITY[1]

Monitoring Project	NADP Precipitation Site[2]	Lat (°N)	Long. (°W)	Years of Record[3]	pH yr^{-1}	SO_4^{-2} dep., kg ha^{-1} yr^{-1}	Precip. Quantity,[4] cm yr^{-1}
Adirondacks, New York	Huntington, NY	43°58'	74°13'	1979-1984	4.36	21.6	99.9
Vermont[5]	Bennington	42°53'	73°10'	1981-1984	4.33	23.0	98.4
Maine	Acadia Park-McFarland Hill	44°22'	68°16'	1982-1984	4.59	22.6	153.0
Upper Midwest	Fernberg, MN	47°57'	91°30'	1981-1984	4.95	8.9	72.9
	Trout Lake, WI	46°03'	89°39'	1980-1984	4.70	14.0	82.8
	Spooner, WI	45°49'	91°52'	1980-1984	4.88	14.0	80.1
	Raco, MI	46°22'	84°45'	1984	4.43	16.9	73.2
Southern Blue Ridge Province	Elkmont, TN	35°40'	83°35'	1981-1984	4.50	26.2	146.3
	Walker Branch, TN	35°58'	84°17'	1980-1984	4.32	28.2	110.4
	Coweeta, NC	35°04'	83°26'	1979-1984	4.60	27.2	182.7
Rocky Mountains, Colorado	Alamosa, CO	37°27'	105°52'	1980-1984	5.49	2.4	16.5
	Mesa Verde, CO	37°12'	108°29'	1981-1984	4.76	6.9	48.4
	Rky Mt Pk, CO	40°17'	105°39'	1984	5.14	7.9	111.1
	Sand Spring, CO	40°30'	107°42'	1979-1984	5.03	4.8	37.8

[1] Data from National Atmospheric Deposition Program, Fort Collins, Colorado (personal communication). Sulfate deposition calculated from precipitation-weighted average SO_4^{-2} and centimeters of precipitation as measured at the site.

[2] Locations of these sites are marked on the regional maps that show LTM lakes (Figures 1-1 through 1-4).

[3] First year of operation included only if data collection exceeded 6 months.

[4] As measured at the NADP site.

[5] Twelve additional bulk precipitation collection sites are operated by the state of Vermont; pH measurement only.

1.2.1 Lake Monitoring in the Northeast

In the Adirondacks, monitoring under the EPA program began in the spring of 1985. Before then, monitoring was conducted by Syracuse University and funded by the Electric Power Research Institute (EPRI). In 1985, EPA began funding Syracuse University to continue monitoring on a monthly schedule. Seventeen lakes (Figure 1-1), comprising a variety of seepage, drainage, and bog lakes, were included in the study set.

The State of Vermont initiated monitoring of 20 lakes in 1981, later expanding the coverage to 36 lakes, of which 24 were sampled in alternate years, for a total of 24 each year, 12 annually and 24 biannually (Figure 1-1). A cooperative agreement was effected in 1982, under which EPA provided partial support for the Vermont program. Sampling has been conducted once per season, including winter, since the program began in 1981. In the spring of 1985, the sampling procedure was changed from integrated column sampling to single epilimnetic and hypolimnetic sampling. This change has caused difficulties in comparing pre- and post-1985 samples, since the integrated column samples occasionally included hypolimnetic water that could influence the sample chemistry.

Six lakes in the Tunk Lake region of Maine were chosen for monitoring in cooperation with the U.S. Fish and Wildlife Service and the University of Maine. These lakes are clustered in a small area not accessible to the public and range from acidic to circumneutral in pH.

1.2.2 Lake Monitoring in the Upper Midwest

In the Upper Midwest, clusters of lakes were selected from surveyed lakes in Minnesota, Wisconsin, and the Upper Peninsula of Michigan (Figure 1-2) that span ANC ranges from near zero to 200 μeq L^{-1} or greater. These lakes were chosen from the results of surveys initiated in 1978 by EPA-Duluth in cooperation with the University of Minnesota-Duluth and the Wisconsin Department of Natural Resources (Glass and Loucks 1986; Schnoor et al. 1986). The University of Minnesota at Minneapolis and the Wisconsin Department of Natural Resources were contracted to continue monitoring beginning in the fall of 1983. Most of the lakes were retained, with a few deletions and additions.

The lakes monitored in the Upper Midwest have the longest period of record of any of the LTM lakes, due to the supplementary data collected and made available by EPA-Duluth. Before 1983, lakes were not sampled on a consistent schedule; since the fall of 1983, over 30 lakes have been sampled seasonally, excluding winter.

1.2.3 Lake Monitoring in the Southeast

Few natural lakes exist in the southeastern United States. However, the TVA has collected extensive data from reservoirs in this area (Figure 1-3). After a survey of 54 reservoirs had been conducted, 12 were chosen for inclusion in the LTM Program. These reservoirs have been sampled seasonally, including winter, since the fall of 1983.

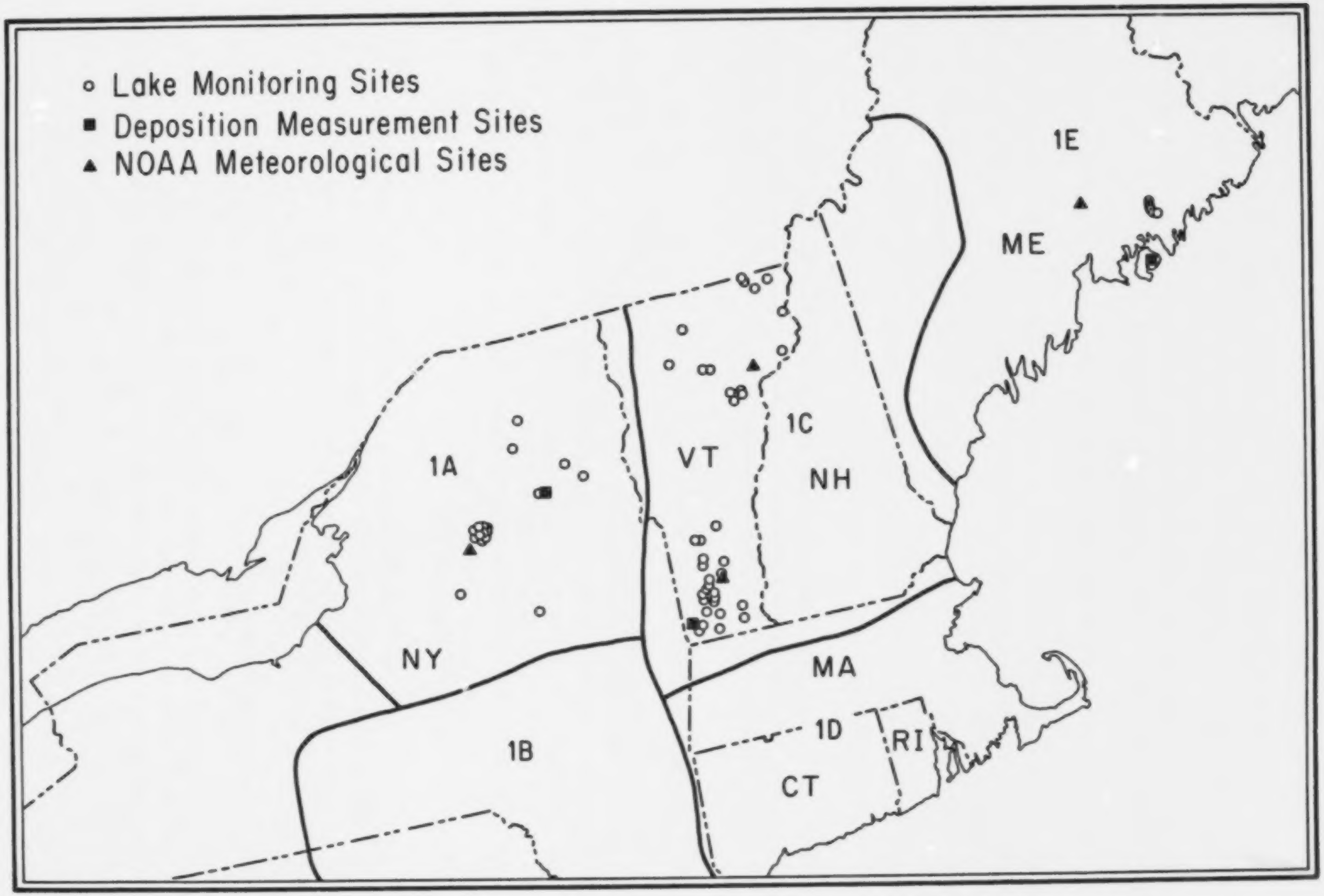

Figure 1-1. Lake monitoring sites, together with proximate deposition measurement and NOAA meteorological sites, in Maine, Vermont, and New York. Boundaries of NSWS subregions 1A - 1E are also shown.

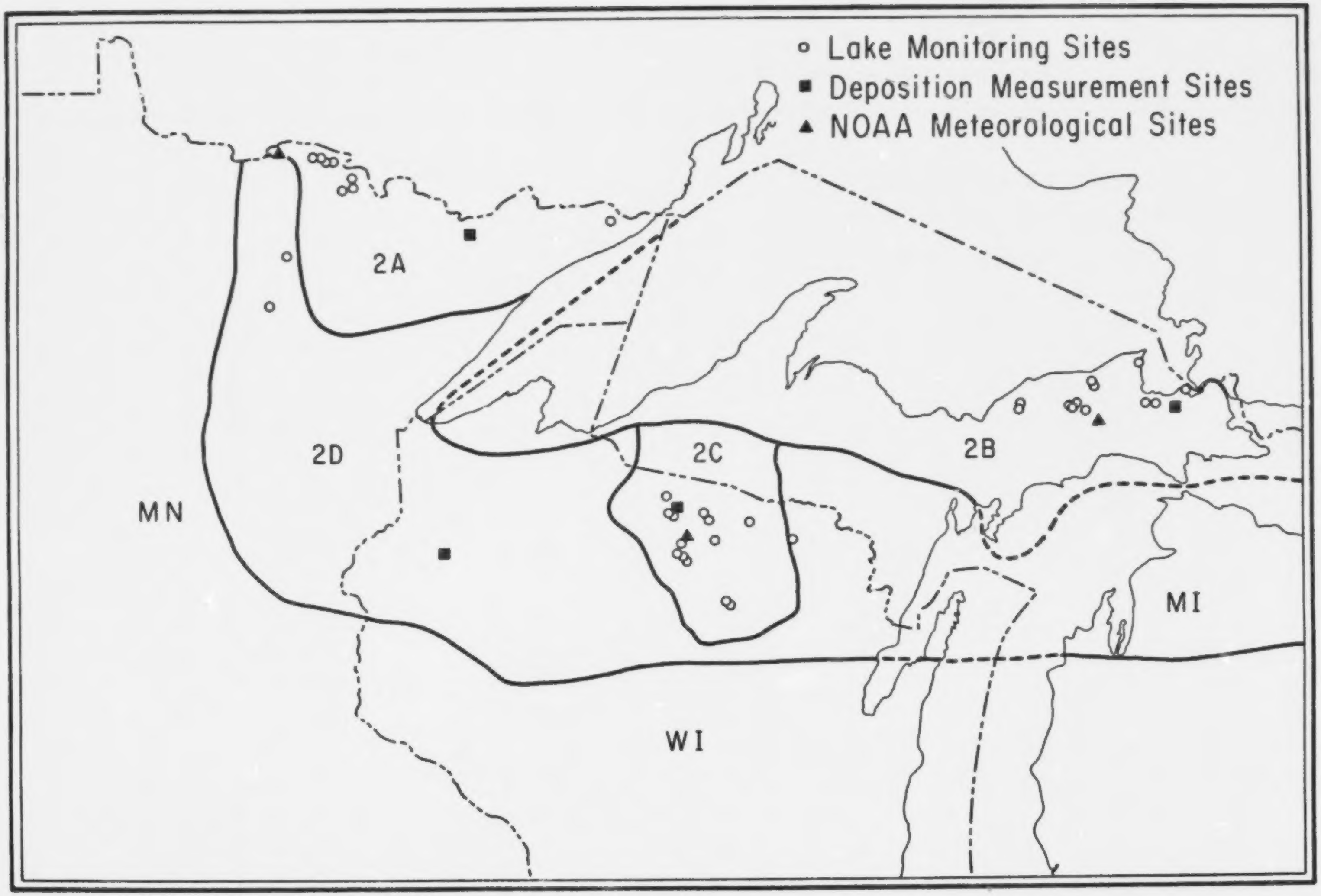

Figure 1-2. Lake monitoring sites, together with proximate deposition measurement and NOAA meteorological sites, in Minnesota, Wisconsin, and Michigan. Boundaries of NSWS subregions 2A - 2D are also shown.

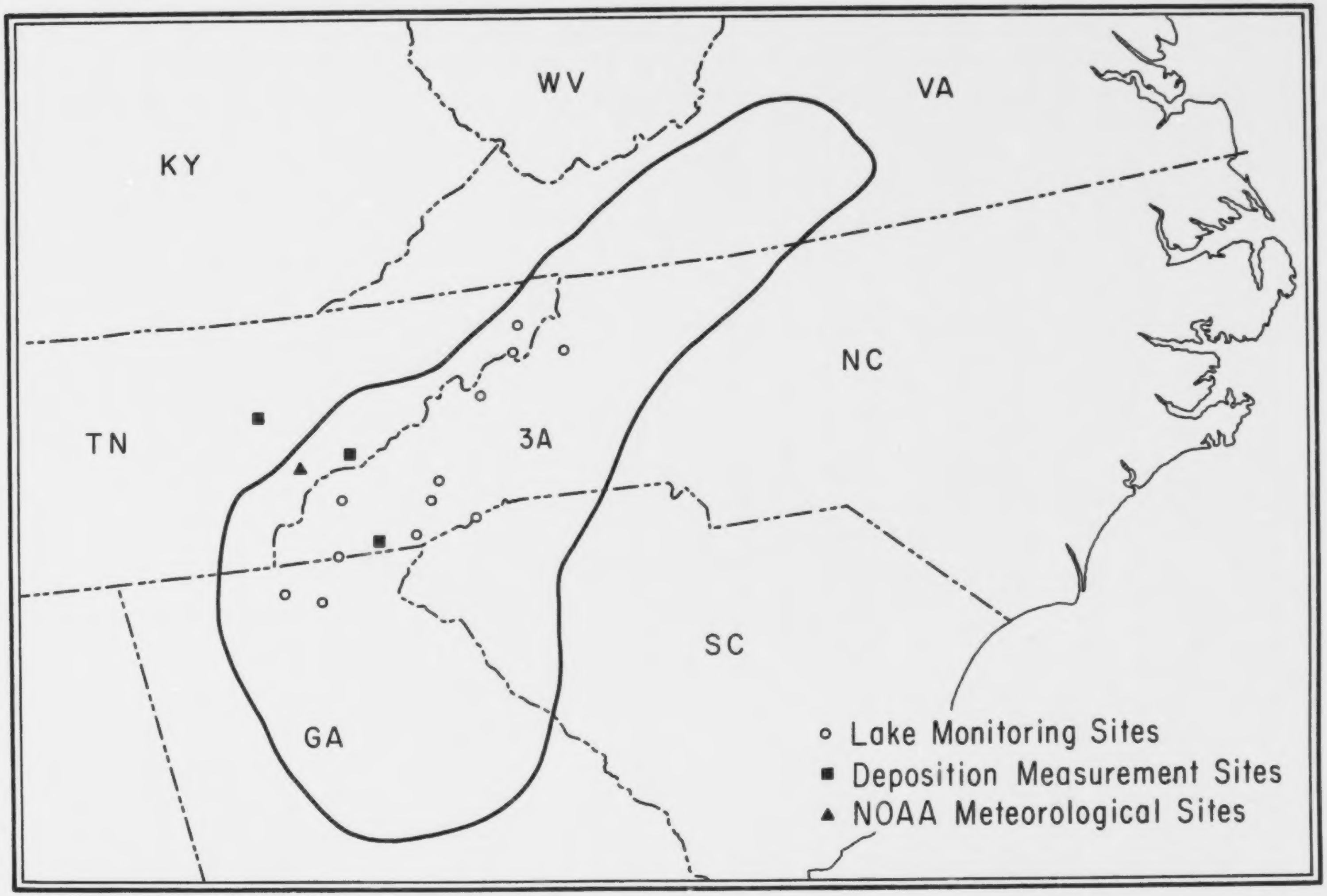

Figure 1-3. Lake monitoring sites, together with proximate deposition measurement and NOAA meteorological sites, in North Carolina, Tennessee, and Georgia (Southern Blue Ridge Province). The boundary of NSWS subregion 3A is also shown.

1.2.4 Lake Monitoring in the Rocky Mountains

In 1985, a cooperative agreement was established with the USGS in cooperation with EPA Region VIII for monitoring 10 lakes in the Mt. Zerkel and Weminuche Wilderness areas of Colorado (Figure 1-4). Located at high elevations, the lakes are covered with ice most of the year and thus are sampled monthly from July through September.

A study of 11 lakes in the northern Rockies was begun in 1983 under a cooperative agreement with Montana State University. It was terminated in 1985 because of continuing problems with data quality that could not be resolved.

1.3 SCOPE AND PURPOSE OF THIS REPORT

1.3.1 Scope

The scope of this report is restricted to the lake monitoring portion of the LTM Program, including data through calendar year 1985. The four stream monitoring projects conducted with USGS and TVA are not discussed in this report; the cooperating agencies are analyzing the data and preparing interpretive reports.

1.3.2 Purpose

In terms of analysis of lake monitoring data, the specific objectives of this report are to:

- Assess the quality of the data
- Determine seasonal and annual variation
- Evaluate the efficiency of the monitoring design
- Describe the relationship of LTM lakes to the population of NSWS lakes
- Examine the data for temporal trends

1.3.3 Questions to be Addressed

Three general issues and several subsidiary ones have been identified for consideration in this report:

- How do LTM lakes compare to other lakes within the same geographic region?
    - Where do LTM lakes fall in the distribution of the lakes included in the NSWS, in terms of specific physical and chemical criteria (lake area, watershed area, pH, ANC, dissolved organic carbon (DOC), etc.)?
    - In terms of chemical characteristics, how do the LTM lakes compare both to each other and to other lakes within the region?
- Are there any trends in the existing data?

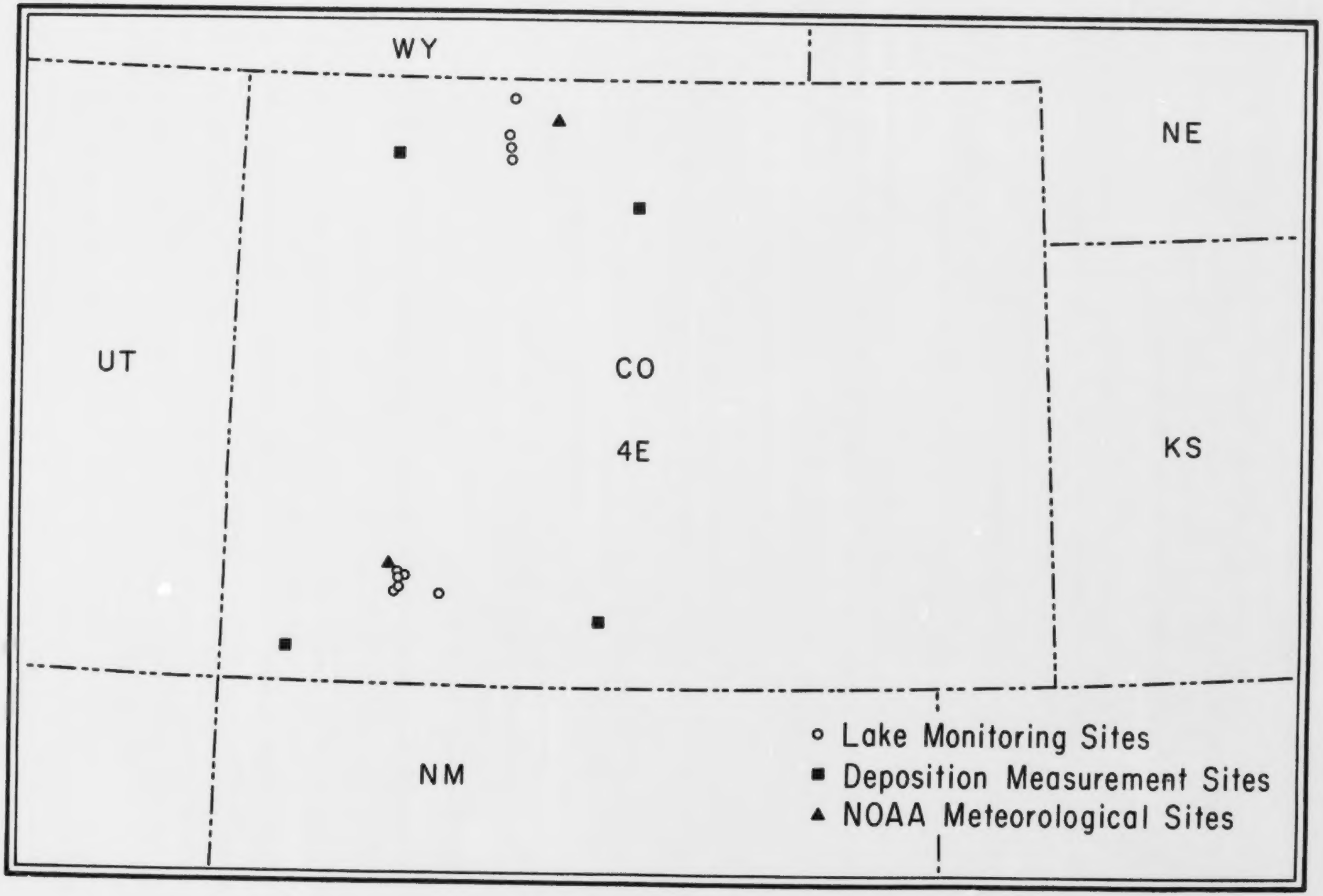

Figure 1-4. Lake monitoring sites, together with proximate deposition measurement and NOAA meteorological sites, in Colorado (Southern Rocky Mountains).

- What can be learned from the design of the current program and how can the information be applied to the optimization of a new monitoring program?
    - Is quality assurance/quality control (QA/QC) adequate? If not, how should it be modified?
    - Are the numbers of lakes sampled in the regions adequate to make inferences concerning regional changes? If not, what projections can be made by analyses of the current program?
    - Can meteorological data help our understanding of lake chemistry?

Addressing these questions will help achieve the goal of providing guidelines for use in designing future programs. This report presents the analyses performed to address these questions and, based on these analyses, provides some guidelines for future programs.

SECTION 2

METHODS

2.1 SAMPLING, ANALYSIS, AND QA/QC PROTOCOLS

As noted in Section 1, the Task Group E ad hoc committee produced a revised draft protocol in 1984 to guide the monitoring effort. However, initiation of the National Lake Survey (NLS) by EPA in the same year resulted in the development of a highly detailed and specific set of sampling, analysis, and quality assurance and quality control (QA/QC) procedures for that project. In order to assure that the monitoring program was in accord with the NLS and in order to take advantage of the more stringent NLS protocols, the original document was modified in May 1985 to incorporate NLS procedures. Laboratory analytical methodology, detection limits, and QA/QC responsibilities (Appendix A) were defined more precisely, and are now very similar to those of the NLS.

2.1.1 Sample Collection

Lake sampling was conducted in the spring as soon after ice-out as possible, in midsummer during the period of thermal stratification, and during the fall turnover. The high elevation Colorado lakes were frozen most of the year; thus, they were sampled during July, August, and September, when ice was not present. Vermont lakes were also sampled in winter, during ice cover, in accordance with their previously established schedule.

Cooperators were provided with protocols specifying that lakes should be sampled near their deepest points, at least 20 m from shore, if possible. If the water column was not thermally stratified, a single sample was collected approximately one-half meter beneath the water surface. If the water body was stratified, a second sample was collected one or two meters above the bottom. There were two exceptions to this procedure. In the Adirondack project, drainage lakes were sampled at their outlets, in order to maintain consistency with the previous RILWAS monitoring program. In the Vermont project, composite water samples were taken until the spring of 1985, when the epilimnion-hypolimnion sampling procedure was initiated. Further details of the sampling protocol can be found in Appendix A.

2.1.2 Measured Chemical Characteristics

The Task Group E committee identified and specified a set of core measurements for all lakes included in the long-term monitoring program (Table 2-1). Additional measurements, including titrated acidity, dissolved inorganic carbon (DIC), dissolved organic carbon (DOC), F, Fe, Mn, NH_4, SiO_2, and total P were made on lakes in the NLS. Some LTM cooperators measured some of these additional variables. Table 2-1 lists the core variables and the methods specified for their analysis. Appendix A provides further details on the laboratory analyses.

TABLE 2-1. ANALYTICAL METHODS FOR CORE VARIABLES USED IN THE EASTERN LAKE SURVEY AND BY THE VARIOUS LTM COOPERATORS.

		Long-Term Monitoring (Cooperators)						
Parameter	National Lake Survey	University of Minnesota	USFWS, Maine	State of Vermont	TVA	Syracuse University	USGS, Denver	References
pH[1]	Orion 611 pH meter.	Combination electrode Corning 476223; Beckman model 071 meter.	Orion 701A and 92e meters; Ross electrodes.	Cole/Parmer Digi-pH-ase meter	Orion SA 250 meter.	Fisher 609 meter. meter.	Orion SA 250	Appendix A
ANC	Gran titration.	Gran titration.	Gran titration.	Gran titration.	Gran titration.	Gran titration.	Gran titration.	Gran, 1950, 1952 Hillman et al., 1986.
CONDUCTIVITY[2]	Wheatstone bridge conductance meter.	Wheatstone bridge conductance meter.	Wheatstone bridge conductance meter.	Wheatstone bridge conductance meter.	Wheatstone bridge conductance meter.	Wheatstone bridge conductance meter.	Radiometer CDM 83 flow-through system.	
COLOR	Hach Model CO-1 Color Determination Kit.	Abs. at 420 nm compared to Pt-Co standard.	Color comparitor, unfiltered sample, Pt-Co standard solution.	Abs. at 420 nm compared to Co-Pt standard.	Chloroplatinate, visual.	Abs. at 420 nm compared to Pt-Co standard.	Color comparitor, unfiltered (settled) sample.	USEPA, 1979.
DOC[2]	Ultraviolet promoted persulfate oxidation, with IR detection.	Photochemical procedure with Barnstead/Syburon carbon analyzer.	(not measured).	(not measured).	Wet oxidation-IR.	Persulfate oxidation, syringe CO_2 stripping, GC.	Dohrman DX 80, direct injection, UV oxidation.	
CA	Acetylene flame atomic absorption, LnCl addition.	Acetylene flame atomic absorption, LnCl addition.	N_2O Acetylene flame atomic absorption,	Acetylene flame atomic absorption, LnCl addition.	Atomic emission-ICP.	Acetylene flame atomic absorption, LnCl addition.	Atomic emission-ICP.	USEPA, 1979.
NA	Acetylene flame atomic absorption.	Acetylene flame atomic absorption.	Acetylene flame atomic absorption.	Acetylene flame atomic absorption.	Acetylene flame atomic absorption.	Acetylene flame atomic absorption.	Atomic emission-ICP.	USEPA, 1979.

[1] A closed system pH was used in the NLS; field pH values were used in the LTM program.

[2] Not a "core" measurement; details on methods are available from each cooperator.

(Continued)

TABLE 2-1. ANALYTICAL METHODS FOR CORE VARIABLES USED IN THE EASTERN LAKE SURVEY AND BY THE VARIOUS LTM COOPERATORS. (Continued)

Parameter	National Lake Survey	University of Minnesota	USFWS, Maine	State of Vermont	TVA	Syracuse University	USGS, Denver	References
K	Acetylene flame atomic absorption.	Acetylene flame atomic absorption.	Acetylene flame atomic absorption.	Acetylene flame atomic absorption.	Acetylene flame atomic absorption.	Acetylene flame atomic absorption.	Acetylene flame atomic absorption.	USEPA, 1979.
MG	Acetylene flame atomic absorption.	Acetylene flame atomic absorption.	N_2O Acetylene flame atomic absorption.	Acetylene flame atomic absorption.	Atomic emission-ICP.	Acetylene flame atomic absorption.	Atomic emission-ICP.	USEPA, 1979.
CL	Ion chromatography.	Ion chromatography.	Ion chromatography.	Automated ferricyanide method. 1985: ion chromatography.	Ion chromatography.	Ion chromatography.	Ion chromatography.	Hillman et al., 1986.
NO_3	Ion chromatography.	Automated cadmium reduction/diazotization method.	Ion chromatography.	Automated cadmium reduction method. 1985: Ion chromatography.	Ion chromatography.	Ion chromatography.	Ion chromatography.	Hillman et al., 1986.
SO_4	Ion chromatography.	Ion chromatography.	Ion chromatography.	Automated methylthymol blue method. 1985: ion chromatography.	Ion chromatography.	Ion chromatography.	Ion chromatography.	Hillman et al., 1986.
AL	Graphite furnace AAS.	Graphite furnace AAS.	Graphite furnace AAS.	Graphite furnace AAS.	Atomic emission. 1985: graphite furnace AAS.	Graphite furnace AAS.	DC plasma spec.	USEPA, 1979.

2.1.3 Quality Assurance

The QA/QC effort for the LTM program was originally the responsibility of the individual LTM cooperators. Following EPA guidelines, each cooperator prepared separate QA/QC plans that were subsequently approved by EPA. In the NLS planning that followed, QA/QC methodologies and protocols were specified and reviewed for use in the surveys (Linthurst et al. 1986; Landers et al. 1987; Drouse et al. 1986). The LTM QA/QC and methodology manual was then revised to comply with NSWS specifications and delivered to all cooperators in May 1985. It provided for the following basic elements:

- In the field, duplicate samples, filtration blanks, and container blanks were obtained at least once for each 10 lakes, sampled as follows:
    - Sampling precision was estimated from duplicates obtained by taking a second lake sample immediately after the first, using exactly the same procedures.
    - Filtration contamination was estimated from deionized water filtration blanks prepared in the field by filtration into properly cleaned anion and cation containers.
    - Container contamination was estimated from an unfiltered container blank prepared by filling a properly cleaned container with deionized water. This sample was analyzed for pH, ANC, and specific conductance.
- In the laboratory, precision was determined by analyzing individual samples in replicate. Accuracy was evaluated in two ways:
    - Analysis of spiked samples prepared by each laboratory with subsequent calculation of percent recovery.
    - Analysis of synthetic audit samples provided by an independent contractor through the EPA.
- At least one on-site field and laboratory evaluation was made for each individual monitoring project by a quality assurance specialist from the EPA's Environmental Research Laboratory, Corvallis, Oregon (ERL-C).

2.2 DATA BASE MANAGEMENT

2.2.1 Data Management

Data management for the LTM data base did not begin until 1985, although data had been collected since 1983 in most regions, and as early as 1981 in others. Thus, LTM investigators had collated their data in a variety of formats. The pre-1985 data came from several sources, including STORET files (Storet User's Handbook, 1985), diskettes provided by cooperators, and hard copies. This lack of consistency greatly increased the complexity of creating the LTM data base, as well as increasing the chances for transcription errors.

In recording sampling data, observation identifiers followed the format for the NLS (Linthurst et al. 1986), in which unique identifiers were assigned to each lake. A unique batch number was assigned to each cooperator for each sampling season. Sample numbers were then assigned to each sample in a batch, so that together the batch and sample identifiers would make up a unique identifier for each observation in the data set. However, cooperators adopted this system at different times in 1984 and 1985, which resulted in a large number of historical observations associated with no unique identifiers.

The difficulty in creating the LTM data base, along with the lack of a set of unique identifiers, increased the potential for errors in the data base and contributed to the creation of a data base that is difficult to update. Encumbered with these problems, the LTM data base was incorporated into a series of SAS files (SAS User's Guide, 1985) in preparation for data analysis in 1986. A tape was prepared at Oak Ridge National Laboratory for use at the USEPA National Computing Center in Research Triangle Park, North Carolina.

2.2.2 Data Verification and Validation

Verification of a data base is the process of confirming that the values in the data base are in fact the values reported from the source of origin. Validation of the data, for the LTM program, is a process of identifying suspect values, based on the history of the data for a given lake, or on a comparison with related chemistry of the same sample.

Verification and validation of the LTM data base was accomplished concurrently with several processes of outlier detection. In one of these, parameters expected to have discernible relationships were regressed using an outlier regression technique that allowed identification of outlying points (Statgraphics, 1986). The regression analyses performed are shown in Table 2-2. Differences between anion and cation sums, and calculated ANC and conductance, were used in the regression analyses, but were not accurate enough to be used as validation criteria, according to NSWS guidelines (Hillman et al. 1986). The lack of DIC data resulted in inaccurate estimates for these parameters.

Univariate analysis (SAS 1985) was also used to detect outliers. In this analysis, distributions of chemical parameters within a given lake over time were described. Outliers were identified as those points having a value more than 3 times the interquartile range from the median.

A data point was flagged as an outlier when it was identified as such using two or more techniques, or when the value was greatly different from any others collected within that lake. The flag indicated whether the data point was higher or lower than expected. To complete the verification, the flagged observations were made known to the cooperators, who then supplied the correctly recorded values or confirmed that the original values were correct. Comparison of these values resulted in the identification of 50 incorrect values out of a total of 101 flagged values in the LTM data base. Fifty-one questionable values remain flagged.

2.3 DATA ANALYSIS METHODS

LTM data were subjected to analyses intended to address the following questions:

1. How do LTM lakes compare to the NLS populations? (Sections 2.3.2, 3.2)

TABLE 2-2. REGRESSION ANALYSIS OF VARIABLE PAIRS TO IDENTIFY OUTLYING OBSERVATIONS

Conductance	vs.	Sum of cations Sum of anions Calcium Calcium plus sodium pH ANC
ANC	vs.	Calcium pH Sum of cations Sum of anions Calculated ANC
pH	vs.	Ratio of SO_4^{-2} to sum of anions
DOC	vs.	Color
Calcium	vs.	Magnesium
Sodium	vs.	Chloride

2. How many lakes should be sampled within a subregion in order to detect a given level of change? (Sections 2.3.3, 3.4.1)
3. How long should monitoring continue in a lake in order to detect a given change? (Sections 2.3.3, 3.4.2)
4. What are the seasonal and annual variations in LTM lakes? (Sections 2.3.5, 3.4.3.1)
5. How much variation among lakes is contributed by season and year effects in the LTM data? (Sections 2.3.5, 3.4.3.2)
6. Which is greater, spring or fall among-lake variation? (Section 2.3.5, 3.4.4)
7. How do fall chemistry values relate to spring values across a subregion? (Sections 2.3.6, 3.4.5)
8. Do meteorological data explain some of the temporal variability in the LTM data? (Sections 2.3.7, 3.5)

The methods used in the data analyses are described in this section. The results are presented and described in Section 3. Implications of the results for the design of future monitoring efforts are discussed in Section 4.2.

2.3.1 Data Used in Analysis

The data used to complete each analysis are shown in Table 2-3. Some data had to be deleted for some of the analyses, because of the limited data available for some regions and some LTM sites. Surface water chemistry was used for all the analyses after elimination of the flagged values. Principal component analysis (PCA) was not completed for the Western Lake Survey (WLS), since only 10 LTM lakes were sampled in the West. Other analyses did not include the Colorado lakes, because data were available for only three monthly sample dates in the summer of 1985. Estimates of the duration of monitoring (question 3; Section 2.3) and the importance of meteorological data (question 8; Section 2.3) were completed only for the Upper Midwest, the Adirondacks, and Vermont, because of the short periods of record for the other regions.

2.3.2 Comparison of LTM Lakes to the NLS Population

As part of the NLS, a survey was conducted of eastern lakes in the fall of 1984 (Linthurst et al. 1986) and of western lakes in the fall of 1985 (Landers et al. 1987). Each lake, chosen statistically from a stratified population, was sampled once during the fall turnover period. The use of weighting factors, derived from the sample selection process, allows extrapolation from the NLS samples to form a description of the chemical characteristics of a defined population of lakes in the regions sampled. Lakes included in the LTM program were chosen individually, with an unknown probability of selection, in clusters of low ANC lakes, and thus may not provide unbiased estimates, even of the populations of low ANC lakes. The results from analysis of the present sample of LTM lakes have not been used to quantify subregional characteristics; however, it is still of interest to demonstrate where the LTM lakes lie with respect to the subregional population distributions.

In order to compare LTM lakes with regional lake populations, three separate approaches were undertaken. In one, values of chemical and physical characteristics of LTM lakes were overlaid on plots of estimated distributions for the NLS subpopulations. This exercise allowed

TABLE 2-3. DATA USED IN STATISTICAL ANALYSES

1.[1] Comparison to NLS	
F(x)	NLS data for the F(x) curves Fall 1984 LTM data for eastern lakes Fall 1985 LTM data for western lakes
Trilinears	NLS data for density contours Fall 1984 LTM data for eastern lakes Fall 1985 LTM data for western lakes
PCA	ELS data for contours ELS data for LTM lakes to represent LTM lakes
2. Number of lakes to be sampled within a region	LTM median seasonal values to estimate among-lake variance[2]
3. Length of time for monitoring to be continued	LTM median seasonal values to estimate within-lake variance[2]
4. Seasonal and annual standard deviations	All surface water LTM data[2]
5. Variability components	LTM median seasonal values[2]
6. Tests for comparing spring and fall variances	LTM median seasonal values[2]
7. Relationship of fall data to spring data	LTM median seasonal values[2]
8. Importance of meteorological data	All surface water LTM data[2], NOAA meteorological data

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[1] These numbers correspond to the questions listed in Section 2.3.

[2] Vermont analyses excluded 1985 data because of the changes in sampling methods and SO_4^{-2} analysis.

comparisons of individual parameters. In a second approach, trilinear plots, containing both NLS population density contours and LTM lakes, provided a comparison of proportional anion and cation composition. Finally, PCA on 13 chemical variables was used to compare LTM lakes to the eastern lakes population for all 13 variables simultaneously. The PCA was not performed for the Western Lakes Survey, so the LTM Colorado lakes were not described by this method. Several years of fall data were available for comparison. However, data from the fall of 1984 for the East and from the fall of 1985 for the West were chosen for the analyses, since data from these seasons corresponded well with NLS data.

2.3.2.1 Distribution Curves--

The distribution curves, F(x), represent estimated cumulative proportions. For any reference value for a variable, F(x) is interpreted as the estimated proportion of lakes in the population having a value less than or equal to the reference value. The LTM lakes were plotted as open circles on the appropriate subregional F(x) curves from the Eastern Lake Survey (ELS) and Western Lake Survey (WLS) data. These results are presented and discussed in Section 3.2.1.

2.3.2.2 Trilinear Plots--

Trilinear plots (Hem 1970) depict relative proportions of the major anions and cations within a lake. Each axis of a triangle represents the percent of one of three major anions or cations. The major anions considered were sulfate, chloride, and ANC. The bicarbonate system, HCO_3^- and CO_3^{-2}, is commonly used on these diagrams. Estimates of these values were not available in the LTM data set, since DIC was not measured. Therefore, ANC was used to approximate the carbonate system. For this use, negative ANC values were set equal to zero, since lakes with negative ANC have negligible carbonate and bicarbonate concentrations. The contribution of organic ions is overlooked in these trilinear plots; no attempt has been made to quantify the magnitude of the organic anion concentrations. The major cations considered were Ca, Mg, and Na + K. These are likely to be a good representation of the major cations in any of the LTM lakes.

2.3.2.3 Principal Component Analysis (PCA)--

PCA was performed on a correlation matrix of 13 chemical variables from the ELS data set. The decision to use a correlation rather than a covariance matrix was based on the disparity in units of some of the variables, such as color or conductance versus concentrations of ions. All variables were expressed as natural logarithms of concentration units. In calculating the correlation matrix, the population weighting factor associated with each lake was employed, so that the resulting correlation estimates the correlations in the ELS population, rather than representing the correlations within the ELS sample. A weighted principal component score was then calculated for each of the ELS lakes. The PCA results were presented graphically as density contour plots of these scores, where the axes correspond to pairs of components (1 and 2, or 2 and 3, etc.) and where the quantity represented in isopleths is an estimate of the percentage of lakes with that score in the ELS population. The same PCA was used to calculate comparable scores for the set of LTM lakes, which were then overlaid on the ELS contour plots for comparison. Interpretation and results of this analysis are presented in Section 3.2.3.

2.3.3 Estimates for Regional Sample Size and Monitoring Duration

A major objective in designing a monitoring program is to ensure that enough samples will be collected to allow trends or changes to be detected at the desired significance level. Two concerns should be kept in mind: the number of lakes sampled across a region must be large enough to enable the characterization of regional changes, and a sufficient number of samples must be taken over time to allow the detection of a change.

Estimates of population variance are required for calculations of sample size, whether the population consists of lakes within a region or of measurements from one lake over time. Determination of the number of lakes that should be sampled in a region or subregion requires an estimate of the variance expected among samples collected from lakes across that region. Determination of the number of samples that must be taken over time within a given lake requires an estimate of the variance expected within the lake over time.

The equations used to estimate optimal sample sizes for ANC, SO_4^{-2}, and pH are presented in the following section. Any or all of these variables are expected to change if deposition loadings change in the future, assuming there is a relationship between atmospheric deposition and lake chemistry.

2.3.4 Equations Used for Estimates

The following equation (Snedecor and Cochran 1980, with slight modification) was used for regional and within-lake sample size calculations for the three primary variables.

$$n = \frac{(Z_{1-\alpha} + Z_{1-\beta})^2 \ \hat{s}_e^2}{\Delta^2} \qquad (1)$$

where n = sample size
$Z_{1-\alpha}$ = Z - score for the desired α level (where α = the probability of a type I error)
$Z_{1-\beta}$ = Z - score for the desired β level (where β = the probability of a type II error)
$\hat{s}_e^2$ = the estimated among-lake variance
Δ = the amount of change

A Type I error occurs in rejecting the null hypothesis when it is in fact correct; a Type II error occurs in not rejecting the null hypothesis when it is in fact false. The probability of avoiding a Type II error is commonly referred to as power. The standard scores from the Z-distribution were used to calculate various levels of significance and power. Combinations of 0.95, 0.9, and 0.8 were chosen for 1-α (type I error or significance level) and 0.95, 0.9, 0.8, and 0.7 for 1-β (Type II error).

Two different variances were estimated: one for among-lake variability and another for within-lake variability. Log transformations were performed on ANC and SO_4^{-2} so that distributions of these variables would approximate normality. Among-lake variability was estimated from the median seasonal values for each subregion. These among-lake variances for each season sampled were averaged, in order to determine an overall among-lake variance for each LTM subregion. These variances were used to estimate the number of lakes to be sampled within a subregion. Within-lake variance was calculated for each LTM lake in the Upper Midwest, the Adirondacks, and Vermont, again using median seasonal values. These variances were used to estimate the number of samples to be taken over time within a given lake.

The amount of change, Δ, was estimated as a percent change for SO_4^{-2} concentration, and for absolute changes in ANC and pH. Percent change refers to detection of a magnitude of change equal to the percent times the mean. The mean refers to the regional mean H^+ or SO_4^{-2} concentration in determining the number of lakes, and to the within-lake mean in determining the number of samples to be collected over time. Percent changes calculated were 50%, 25%, and 10% increase or decrease. For low values of ANC, which are of greatest interest, a 10% change would be much smaller than the analytical precision of ANC measurements. Thus, sample sizes were calculated for absolute changes of 10, 25, and 50 μeq l^{-1} in ANC, for both the across-region and within-lake sample sizes. Absolute changes in pH of 0.5, 0.35, and 0.2 pH units correspond to changes in H^+ concentrations of 310%, 225%, and 160%.

The equation was modified for calculation of the number of samples to be collected over time, in order to account for serial correlation, by adding the $1-\theta$ and $1+\theta$ terms:

$$n = \frac{(Z_{1-\alpha} + Z_{1-\beta})^2(1+\theta)\hat{s}_e^2}{\Delta^2(1-\theta)} \qquad (2)$$

where n = sample size
$Z_{1-\alpha}$ = Z-score for the desired α level
$Z_{1-\beta}$ = Z-score for the desired β level
θ = serial correlation coefficient
$\hat{s}_e^2$ = the estimated within-lake variance
Δ = the amount of change detected.

Serial correlation is usually present when samples are taken from a single source over time, when the recent past influences the current measurement. Such correlation was demonstrated in the Upper Midwest, the Adirondacks, and the Vermont LTM data. The value of this coefficient was estimated by first order autoregression at 0.9 in the Adirondack data, and at 0.84, 0.88, and 0.63 for ANC, pH, and SO_4^{-2} in the Vermont data. Estimation of the correlation coefficient for the Upper Midwest was much more difficult, because of the inconsistent sampling schedule, but it was estimated to lie between 0.26 and 0.5. The value 0.4 was chosen arbitrarily to represent θ in the Upper Midwest for this analysis.

2.3.5 Variability

Several analyses were completed to describe seasonal and annual variability in the LTM data. Standard deviations of median seasonal values were calculated for the groups of LTM lakes within each subregion on the following basis:

- The standard deviation among years as the standard deviation of annual mean values for a given parameter.
- The standard deviation within years as the mean of the standard deviations about each annual mean.
- The standard deviation among seasons as the standard deviation about the seasonal mean values for the parameters in question.
- The standard deviation within seasons as the mean of the standard deviations about the seasonal means for each parameter.

These were calculated for each subregion from the median seasonal values for each lake across the subregion.

Analysis of variance was used to estimate the proportion of variance accounted for by the differences among lakes within a region, and by annual and seasonal variability. The analysis was set up using the following model:

$$Y_{ijk} = \mu + \alpha_i + \beta_j + \eta_{k(j)} + \alpha\beta_{ij} + \alpha\eta_{ik(j)} \qquad (3)$$

where:

Y_{ijk} = Median seasonal values for ANC, pH, SO_4^{-2}
μ = overall mean
α_i = lake effect
β_j = year effect
$\eta_{k(j)}$ = seasonal effect (nested within year)
$\alpha\beta_{ij}$ = lake-by-year interaction
$\alpha\eta_{ik(j)}$ = lake-by-season interaction

This model included interaction terms, as these effects account for different levels of annual or seasonal change among the lakes. Exclusion of these terms assumes that all lakes across a region undergo the same change from one season to the next. This model provides a complete classification of the data without an error term.

Proportions of the total variance explained by each component were determined by dividing the sum of squares due to each effect by the total sum of squares of the model. These proportions sum to 1.0, since no error term was included in the model.

Spring and fall variances were compared to determine whether among-lake variances for these seasons differed. Tiku's robust test (Tiku 1986; Tiku and Balakrishnan 1984) was used for this analysis because it is robust against departures from normality. The more well-known F-test is extremely sensitive to small departures from normality (Miller, 1981; Snedecor and Cochran, 1980). Examination of the LTM data suggested a departure from normality.

2.3.6 Fall Index

In the National Lake Survey project, lakes were sampled one time only, in the fall. Logistically, sampling at the fall turnover period was easier than sampling during spring turnover, which could occur soon after an unpredictable ice-out. Additionally, lakes were considered to be less variable in the fall, since fall turnover periods are usually longer than spring turnover. LTM data were collected monthly or seasonally and have been used to investigate some of these assumptions.

To describe the relationship of the fall sample to the other seasons, correlations of fall values with spring, summer, or winter values from the same lakes were assessed. The high correlations observed prompted further analysis to describe the spring-fall relationships for ANC, pH, SO_4^{-2}, and Ca. General linear models were constructed to test whether the relationships differed among subregions and years. When differences among subregions were found to be significant, further tests were done strictly on a subregional basis.

The following models were used for these tests. To test whether subregions were characterized by different relationships, data from all the subregions were combined, and the following model was applied:

$$Y_i = \beta_0 + \beta_1 X_i + \beta_2 Z_j + \beta_3 XZ_{ij} + \epsilon_{ij} \qquad (4)$$

where Y_i = spring value
X_i = fall value
Z_j = subregion
XZ_{ij} = fall value-by-subregion interaction

where subregion was a classification or indicator variable such that a significant effect of subregion alone would indicate the presence of parallel relationships of differing intercepts, whereas a significant contribution of the fall value-by-subregion interaction term indicates that the slope changes among subregions (Neter et al. 1983).

This test showed significant differences among subregions, so further evaluation of the relationships across years was done separately for each subregion. The model used to evaluate this effect was similar:

$$Y_i = \beta_0 + \beta_1 X_i + \beta_2 Q_k + \beta_3 XQ_{ik} + \epsilon_{ik} \qquad (5)$$

where Y_i = spring value
X_i = fall value
Q_k = year
XQ_{ik} = fall value by year interaction

again with year as a classification variable, significance of the year term alone indicating parallel slopes with different intercepts for some years, and the year-by-fall interaction term indicating different slopes among years.

2.3.7 Importance of Meteorological Data

A general linear model was used to evaluate how much additional variability could be explained by precipitation and temperature data. Precipitation and temperature data were observed from National Oceanographic and Atmospheric Administration (NOAA) (1978-1985) records from sites in the vicinity of the LTM lakes (see Figures 1-1 to 1-4). A general linear model of the following form was used:

$$Y_{ijkl} = \mu + \alpha_i + \alpha\eta_{ik} + P_{ijkl} + LP_{ijkl} + T_{ijkl} + LT_{ijkl} + \beta_j + \eta_{k(j)} + \epsilon_{ijk} \quad (6)$$

where Y_{ijkl} = ANC, pH, SO_4^{-2}, or Ca
μ = overall mean
α_i = lake identification
$\alpha\eta_{ik}$ = lake-by-season interaction
P_{ijkl} = precipitation in the month of sampling
LP_{ijkl} = precipitation in the month prior to sampling
T_{ijkl} = average air temperature in the month of sampling
LT_{ijkl} = average air temperature in the month prior to sampling
β_j = year
$\eta_{k(j)}$ = season effect nested within year

The lake by season interaction term accounts for the variable change from one lake to the next across seasons.

The effect of including precipitation and air temperature in the model was assessed in two ways. As in the model presented in Section 2.3.4, the proportion of the total sum of squares was calculated. Additionally, autocorrelation of the residuals was determined with and without inclusion of the meteorological data in the model, as inclusion of these terms was found to affect the fit of the model.

SECTION 3

RESULTS AND DISCUSSION

3.1 QUALITY ASSURANCE AND QUALITY CONTROL (QA/QC)

The analysis of quality assurance samples from the Long-Term Monitoring (LTM) Program provided an opportunity for estimating the quality of the data, including its precision and accuracy. Field blanks were used to estimate the background values for each parameter, including both the analytical detection limit of a particular method and the potential for sample contamination during collection and processing. The results of the field blank evaluations are presented in Table 3-1 as upper confidence bounds for blank analyses. These were calculated as the 95th percentile of the distribution of field blank measurements for all laboratories (Best et al. 1986). All data were combined for this analysis, since the number of blank analyses was too small to allow analysis of variance for the determination of field blank values for each laboratory for each year or each sampling period. This is unfortunate, as a cursory examination of the data suggests that there are differences among laboratories and sampling dates.

The results of sample duplicate analyses were used to evaluate analytical precision, including the variability associated both with sample collection and with routine processing. Precision estimates are presented as standard deviations in Table 3-2. These standard deviations are based on sample sizes ranging from 2 to 14, with all data collected over the year combined. Sample sizes were too small to calculate precision for each field season. Blank values for NO_3^- and total Al were extremely high. Thus, although these parameters are of interest, LTM data for these variables were not used in the analyses. These values reflect low relative percent standard deviations (s.d. divided by the mean, multiplied by 100), in general below 5% for cations and below 10% for anions. No data quality objectives were adopted for the LTM project; however, these values are within the QA objectives outlined for the National Lake Survey by Drouse et al. (1986).

Interlaboratory bias was evaluated by comparing individual laboratory measurements of synthetic audits (supplied by Radian Corporation, Austin, Texas) with Radian's theoretical values, or with Radian's analyses of their own audit samples. Bias is presented as a percent and was calculated as the difference between the laboratory value and a known value, such as the theoretical value, divided by the known value. Figures 3-1 and 3-2 show the data. Relative bias for analyses of synthetic audit samples ranged from -100 to 110%, and was further investigated by analysis of variance. No significant effect was found for either laboratory or chemical parameters; equal bias was found among laboratories, and no parameter was consistently analyzed with greater bias than another.

Since no significant differences were found within any particular laboratory or parameter, the relative bias data were pooled to calculate an average bias with corresponding 95% confidence intervals. The mean bias for all variables was 0.29% ± 34.8. This interval suggests that the mean bias is not significantly different from zero, but that the confidence interval is very large, indicating that interlaboratory variation is too high for any conclusions to be drawn about bias.

TABLE 3-1. POOLED RESULTS OF FIELD BLANK ANALYSES FOR ALL LABORATORIES INCLUDED IN THE LONG-TERM MONITORING PROGRAM

Parameter Unit	Sample Size	Upper Confidence Bound of Blanks[1]
ANC (μeq L^{-1})	32	18.00
Conductance (μS cm^{-1})	33	3.00
Ca (μeq L^{-1})	88	13.47
Mg (μeq L^{-1})	87	2.49
Na (μeq L^{-1})	91	43.50
K (μeq L^{-1})	87	0.00
SO_4^{-2} (μeq L^{-1})	69	0.00
Cl^- (μeq L^{-1})	70	0.56
NO_3^- (μeq L^{-1})	71	571.12
Al (μg L^{-1})	67	33.00

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[1] Presented as the 95th percentile of the distribution of field blank measurements for all laboratories.

TABLE 3-2. PRECISION DATA FOR LTM PROJECTS, PRESENTED AS THE STANDARD DEVIATION OF DUPLICATE ANALYSES (IN μeq L^{-1} FOR ALL PARAMETERS EXCEPT pH AND CONDUCTANCE) (Blank cells indicate no available data.)

	Parameters									
Labs/Yr.	Ca	Mg	K	Na	Cl^-	SO_4^{-2}	NO_3^-	pH	ANC	Cond.
A[1]										
1983										
1984										
1985	1.497	0.414	0.256	0.000	0.000	1.040		0.050	7.500	0.100
B										
1983	6.936	0.829	0.511	1.784				0.040	0.017	0.601
1984	1.397	0.994	0.639	0.783	1.579	1.623	0.214	0.030	0.093	
1985	1.148	0.166	2.378	1.000	3.666	1.103		0.029	7.290	0.330
C										
1983	1.198	0.331	0.128	1.044				0.034	0.794	
1984										
1985										
D										
1983	1.896	6.629	0.281	15.921	2.115	0.812	478.313	0.039	10.300	0.517
1984	12.325	2.403	1.304	8.482	0.649	2.206	539.708	0.047	11.400	0.329
1985	4.790	2.486	0.384	1.305	3.384	2.705		0.015	3.370	0.342
E										
1985	0.250	0.000	0.000	0.087	0.000	0.354		0.009	0.384	0.048
F										
1985	2.295	3.812	0.179	0.740	5.640	0.416		0.000	3.308	0.316

[1] A-F represent the various LTM cooperating laboratories.

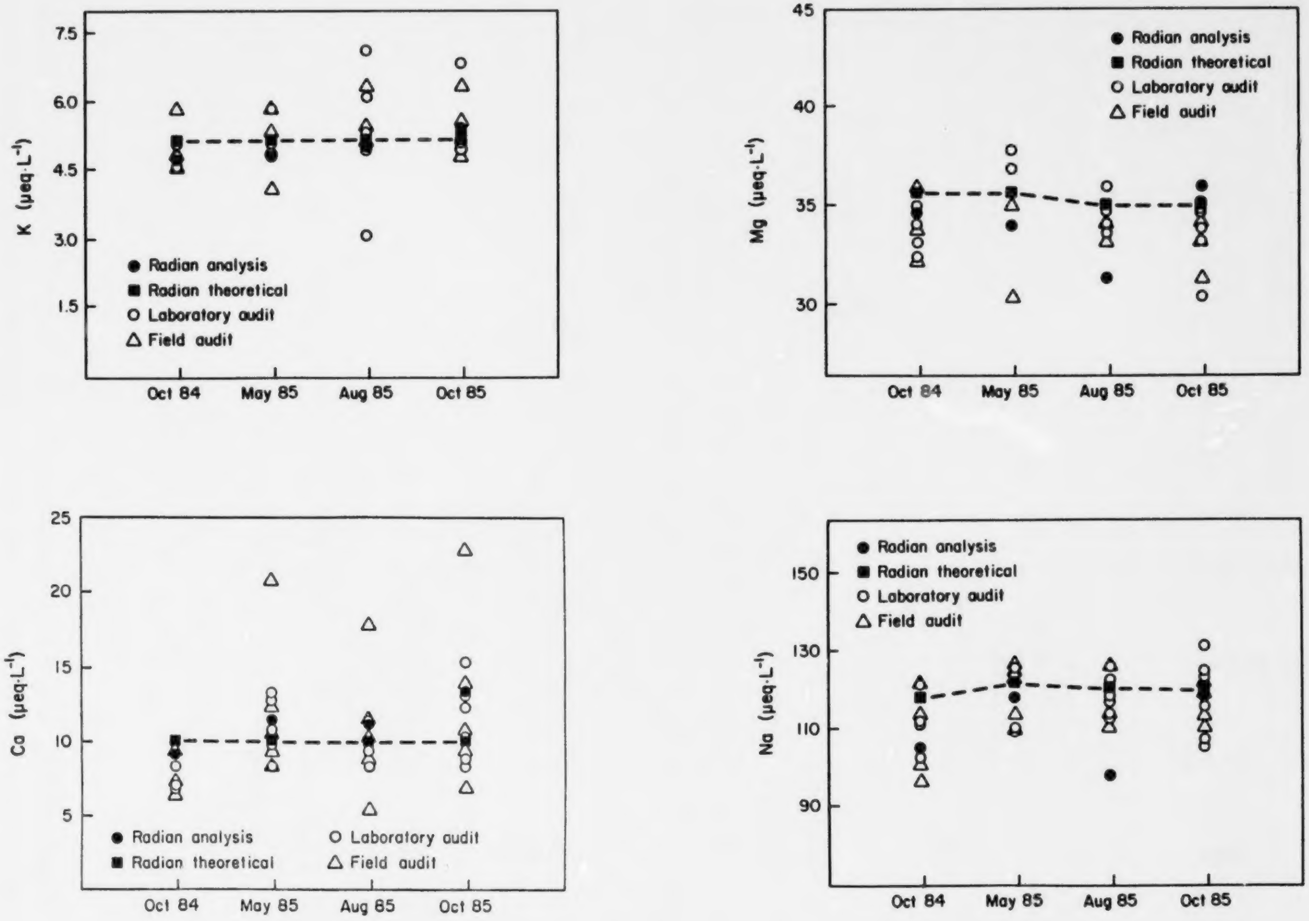


Figure 3-1. Cation analysis of synthetic audit samples showing theoretical values, Radian analysis results, and LTM field and laboratory audit samples for Ca, Mg, Na, and K. The dashed line identifies the Radian theoretical values.

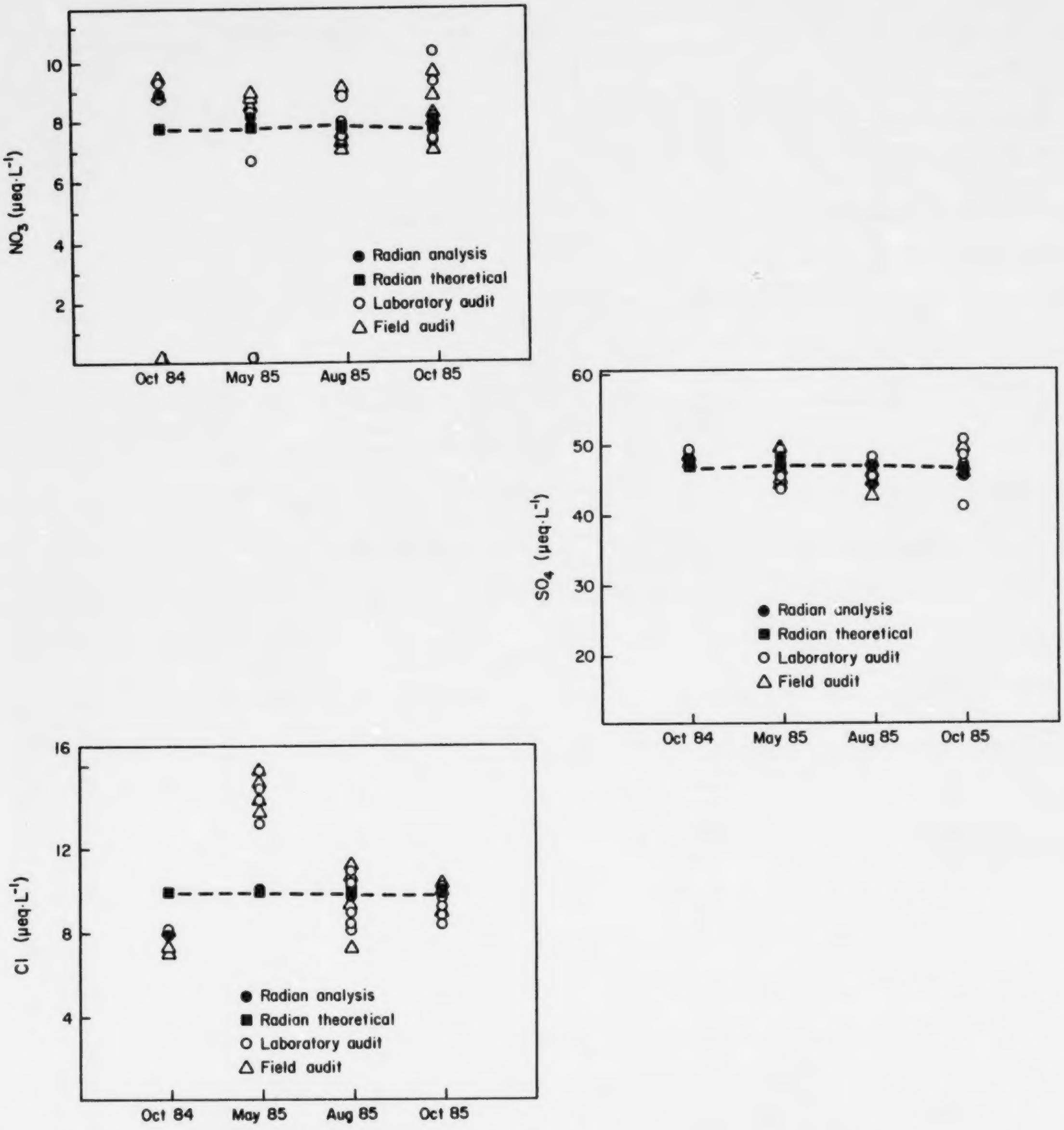


Figure 3-2. Anion analysis of synthetic audit samples showing theoretical values, Radian analysis results, and LTM field and laboratory audit samples for NO_3^-, SO_4^{-2}, and Cl^-. The dashed line identifies the Radian theoretical values.

Plots of field and laboratory audit results over time (Figures 3-1 and 3-2) support the analysis of variance results. Laboratory and field results from the LTM cooperators are shown as open symbols, while the Radian laboratory and theoretical values are shown as solid symbols. The dotted line connects the theoretical values over time. The figures thus give a visual representation of the comparison of individual laboratory performance to the Radian theoretical or laboratory values.

There is a consistent spread of the data about the theoretical values for both anions and cations, with the exception of chloride. For the first two audit samples, chloride was below and then above the theoretical concentrations for the laboratory samples, but not for the field samples. Because field and laboratory samples overlap in a wide range, there is again no indication of predictable bias.

The bias calculations for each laboratory were based on the theoretical audit sample concentrations. Theoretical concentrations are based on gravimetric measurements of reagents and salts used to prepare the sample, which may not be an accurate prediction of analytical results and do not account for incomplete solubility, holding times, or analytical precision.

The contracting laboratory that analyzed the samples showed no better performance than the LTM cooperators. In addition, the synthetic audit samples were diluted from a concentrated solution on the day samples were shipped. All LTM cooperators received samples prepared on the same day, so for a given LTM audit, all samples should have been the same. However, these were not necessarily the same dilutions analyzed and reported by the contracting laboratory. In addition, cooperators may have analyzed them on different dates, resulting in different holding times.

Radian audit samples of the same lot numbers were analyzed in the National Surface Water Survey (NSWS) Program as well; audits analyzed for the Eastern Lake Survey (ELS), the Stream Pilot Study, and the Western Lake Survey (WLS) were from the same lots as the October 1984 and May and October 1985 LTM audits, respectively. A comparison of the means of the NSWS data to the LTM data indicates that the LTM data were closer to the Radian theoretical values 71% of the time. The NSWS QA/QC plans required reanalysis of samples when analyses of audits deviated more than ± 10% from the theoretical values and other deviations were discovered. The most accurate of these samples were then entered into the final data base, so that the NSWS audit results may be biased toward the Radian theoretical values. Thus, it appears that the LTM laboratories performed as well as other laboratories that analyzed the Radian synthetic audit samples, so the high variation demonstrated may be more accurately attributed to the unstable synthetic audit samples than to poor laboratory performance.

For audit samples to be good indicators of analytical performance, the concentrations of the audit samples should be similar to concentrations in the samples of interest. A comparison of the concentration of the audit samples to ranges found in the LTM lakes showed that Na and NO_3^- concentrations were two to three times higher than were average lake concentrations. The remaining parameters corresponded well with average lake concentrations. This comparison suggests that the synthetic audit samples contained reasonable levels of the analytes of interest.

Inspection of results from spiked samples, spikes of nanopure water, and other quality control samples presented by individual investigators showed average bias calculations of less than 10% for all parameters. Generally, all observations had a bias of less than 10%, with an occasional outlier of higher bias. All mean interlaboratory bias values were less than 10%.

The QA/QC data as a whole indicate that the laboratories involved in the LTM Program demonstrate a high level of precision (less than 10% RSD), an average overall bias of ± 10%, according to self-prepared spiked samples, and 0.29% ± 34.8%, based on the Radian audit sample analysis.

3.2 COMPARISON OF LTM LAKES TO THE NLS POPULATION

3.2.1 Comparison to Cumulative Distribution Frequencies

Inspection of cumulative distribution frequency curves (F(x) curves) for ANC (Figure 3-3) shows that most LTM lakes in Vermont and Maine fall on the lower half of the curve, indicating that LTM lakes are lower in ANC than the NLS population medians. A complete set of F(x) curves is included in Appendix C. F(x) curves for ANC, pH, SO_4^{-2}, Ca, color, and site depth are included here (Figures 3-3 and 3-4) only for Vermont (1C) and Maine (1E), in order to highlight the limited distribution of the LTM Maine lakes for these characteristics. In general, the other subregions had distributions similar to that of Vermont. In Maine (1E), the LTM lakes are characterized by ANC values as low as 20% of those of the ELS populations. The distribution of LTM lakes compared to the ELS distribution in Vermont is similar to that seen in most subregions and is shown in Figures 3-3 and 3-4 as an example. In Northeastern Minnesota (2A) and Southern Appalachians (3A), one or two of the lakes have a high ANC (> 200 μeq L^{-1}). Not surprisingly, pH and Ca follow a distribution similar to that of ANC among all subregions. These variables correlate with ANC (Henriksen 1979).

LTM lakes generally had sulfate values as high as the 80th percentile in each subregion. However, only in the Southern Appalachians (3A), were lakes distributed across the range of sulfate values. Most of the other regions did not have lakes with low sulfate concentrations. Lakes in Colorado had absolute sulfate concentrations lower than those of other regions, but they compare to the subregional population distribution in a similar way, due to the lower sulfate concentrations found in western lakes (Landers et al. 1987).

LTM lakes were generally low in dissolved organic carbon (DOC), with lakes in most subregions below the subregional median value. Exceptions to this occurred in the Adirondacks (1A) and Vermont (1C), where LTM lakes appear to be spread over the subregional ranges of DOC and color, respectively. In Colorado (4E), the three lakes for which DOC data were available had relatively high values of DOC.

Watershed areas and lake areas of the LTM lakes in the Northeast and Upper Midwest span the ranges of the ELS populations for these regions. In the Southern Appalachians (3A), 4 of the 12 LTM lakes had large lake areas (> 2000 ha, the cutoff for lakes in the ELS), and correspondingly large watershed areas. These large lakes demonstrated no particular bias with respect to the chemical parameters, suggesting that large lakes may have chemical characteristics of interest in long-term monitoring.

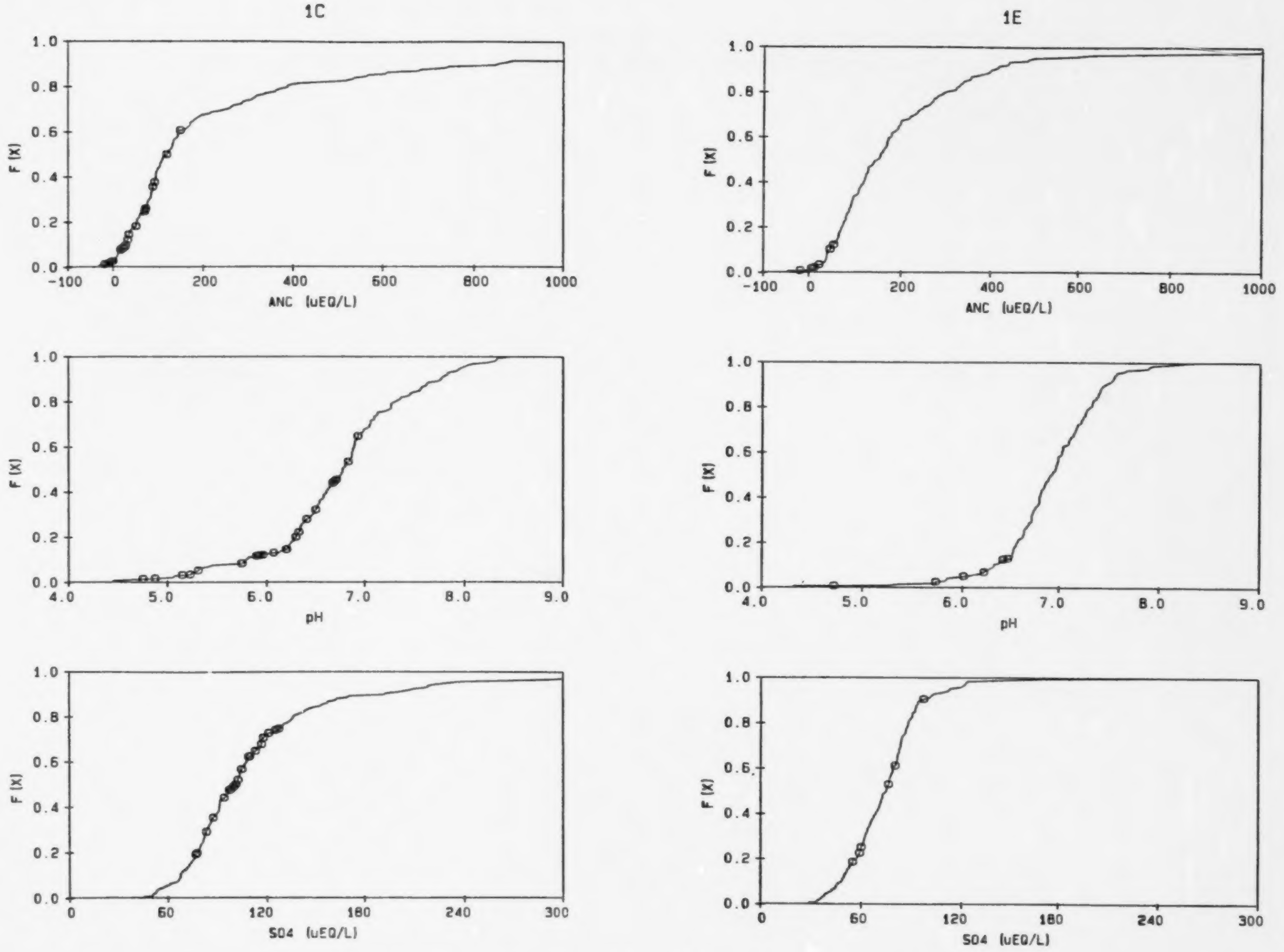


Figure 3-3. F(x) curves for ANC, pH, and SO_4^{-2} from the Eastern Lakes Survey data for Central New England (1C) and Maine (1E). LTM lakes in these subregions are indicated as open circles.

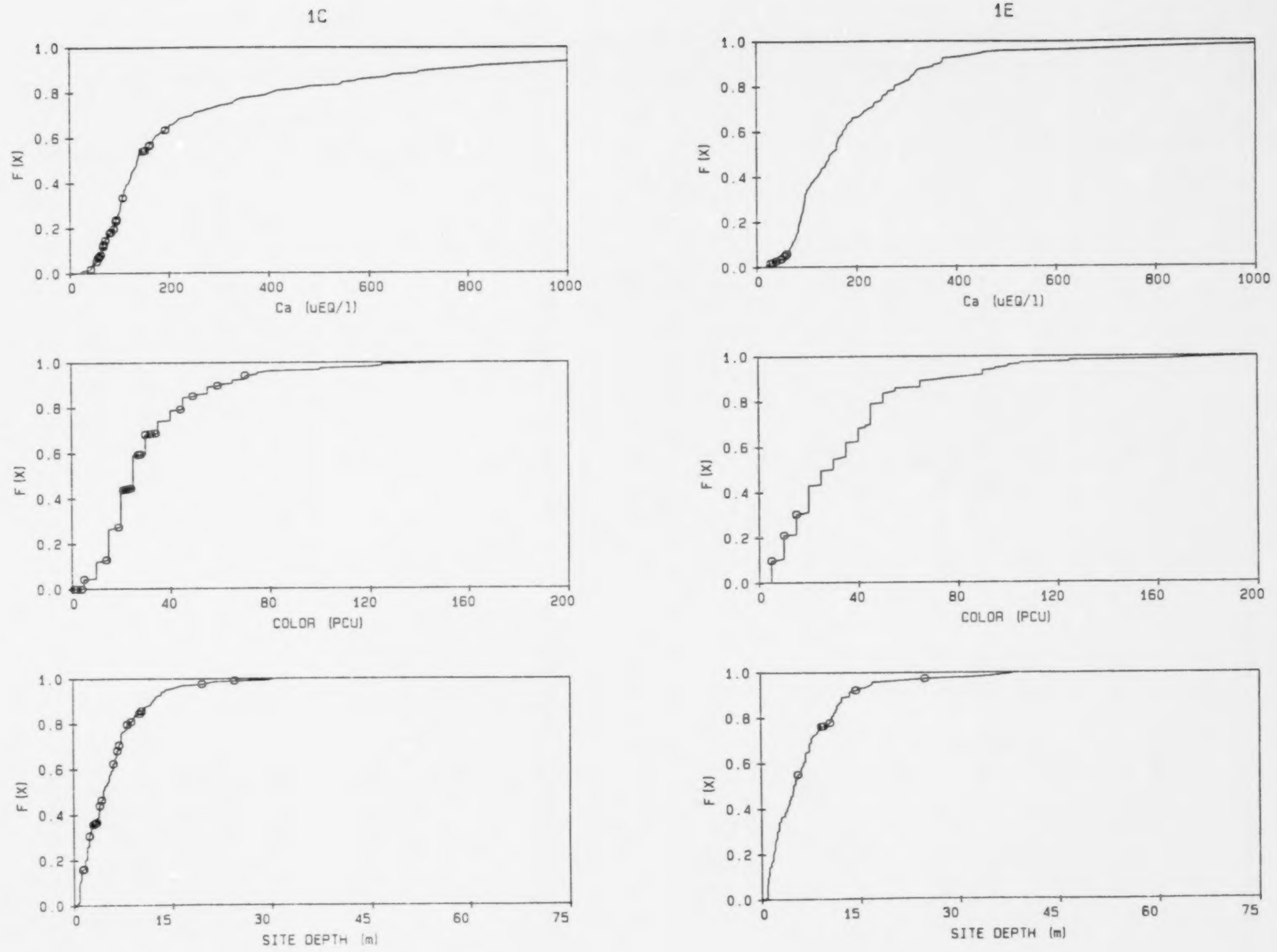


Figure 3-4. F(x) curves for Ca, color, and site depth from the Eastern Lakes Survey data for Central New England (1C) and Maine (1E). LTM lakes in these subregions are indicated as open circles.

3.2.2 Comparison to ELS Subregional Trilinear Plots

3.2.2.1 Interpretation of Trilinear Plots--

This subsection explains how to interpret the trilinear plots; a more in-depth discussion can be found in Fetter (1980). In Figures 3-5 through 3-7, each axis of the larger triangle is scaled by the proportion of that ion present in the sample. The anion and cation triangles have been subdivided into four smaller triangles. The triangle is subdivided by connecting the midpoints of each axis. Dominance is defined as one ion comprising more than 50% of the total anion or cation composition. The three resulting corner triangles thus represent regions in which each anion or cation dominates the system. A lake falling in the gray region is one in which all of the major ions are present at less than 50% of the total composition; thus no single ion is dominant in the system. A simple key to interpretation is:

- Upper triangle is dominated by Mg or SO_4^{-2}
- Lower left triangle is dominated by Ca or ANC (bicarbonate system)
- Lower right triangle is dominated by Na + K or Cl^-
- Gray triangle has no dominant cation or anion

These diagrams were constructed with the assumption that cations other than the base cations Ca, Mg, Na, and K were negligible components of the ionic makeup. Neither were organic anions considered in producing these plots, and they may have been important in some lakes, although, given the low DOC concentrations overall, this is unlikely. Nitrate, an important anion in many aquatic systems, was also ignored in this analysis, as it occurred in very low concentrations.

Population density contours of the NLS populations are also shown on the trilinear plots. These contours represent the 80th, 50th, 20th, and 5th percentiles of the population density. Thus, the center of a series of concentric rings identifies a mode of the subregional population, the mode being an area of high density. These percentiles refer to the density of lakes only, and should not be construed as percentiles of the population distribution, such as are indicated by the F(x) curves. For ease in comparing the LTM lakes to the subregional populations, the percent of the NLS population occurring in each of the four smaller triangles is indicated in the smaller triangles to the right of the trilinear diagrams.

3.2.2.2 Subregional Comparison of LTM Trilinear Results to NLS--

All but two of the LTM Adirondack lakes are sulfate dominated (Figure 3-5), as is 50% of the NLS population. The two are carbonate dominated, with low Cl^- contributions. LTM lakes are Ca dominated, as is 88% of the ELS population. LTM lakes in the Adirondacks are thus mainly described as $CaSO_4$ lakes, while both $CaSO_4$ and $Ca(HCO_3)_2$ lakes occur in this subregion.

A similar pattern is seen in the Vermont LTM lakes. Most of these are sulfate dominated, while only 27% of the NLS population is SO_4 dominated. ANC dominant lakes comprise the largest percentage (32%), with a significant contribution of nondominated lakes. LTM lakes are split between Ca dominated and no dominant cation, as are the ELS lakes in Central New England.

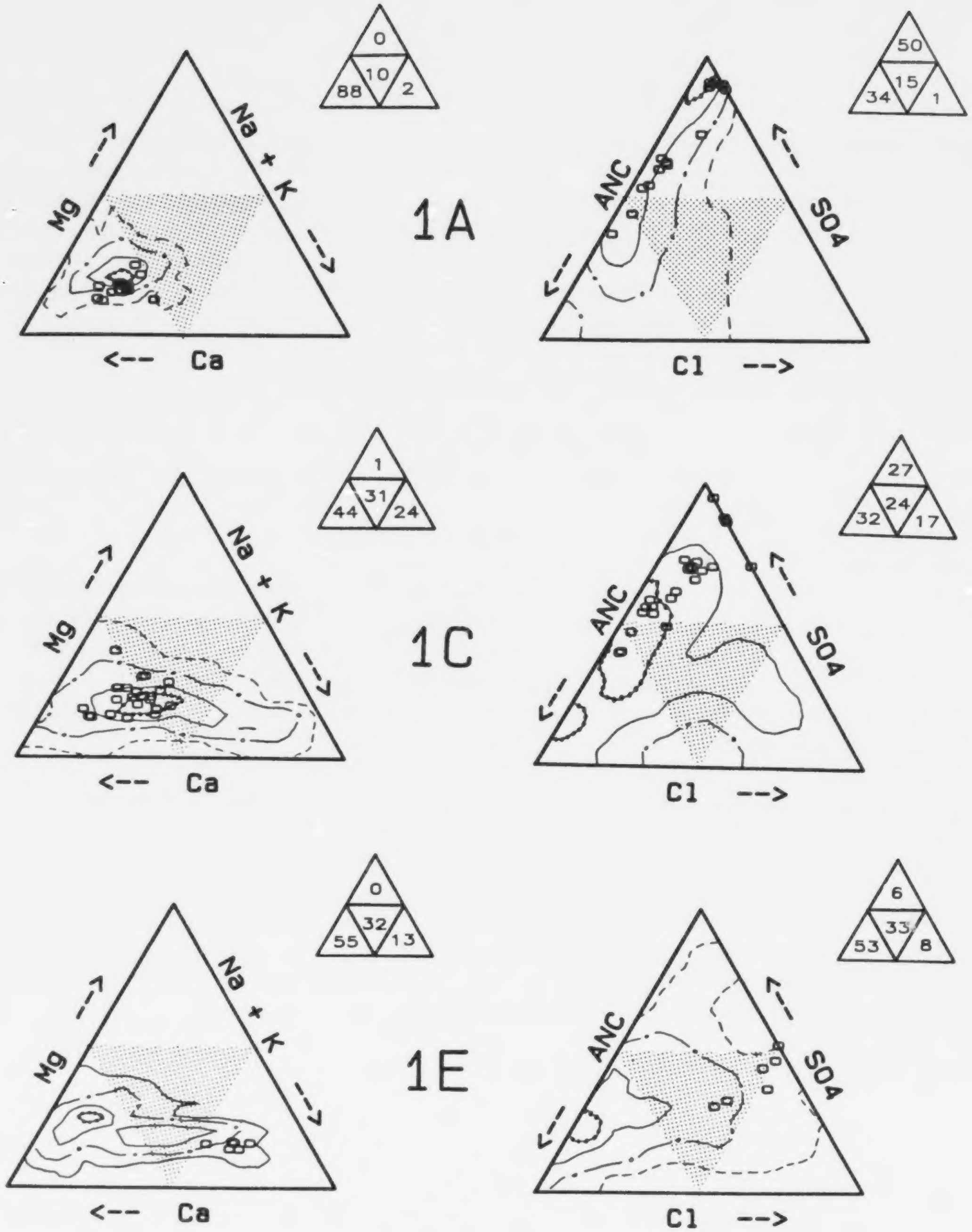


Figure 3-5. Trilinear diagrams for anions and cations for the Adirondacks (1A), Central New England (1C), and Maine (1E). Open circles represent LTM lakes, while dashed and dotted lines indicate percentiles of the ELS population density. (•–•–• 80th; ⁀ 50th; •—• 20th; ---- 5th). The smaller triangles to the right of the trilinears indicate the percent of the ELS population found in each of the subtriangles.

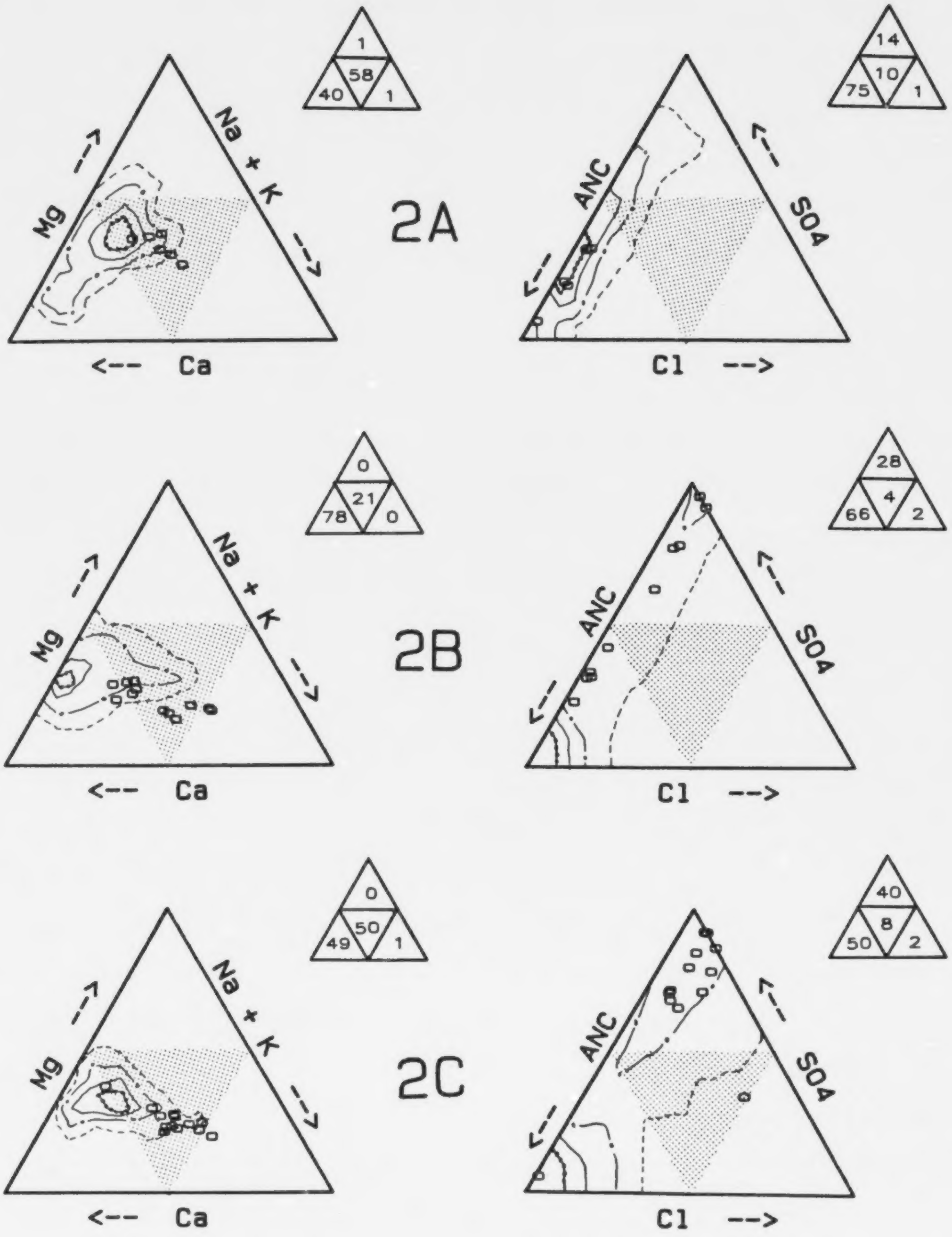


Figure 3-6. Trilinear diagrams for anions and cations for Northeastern Minnesota (2A), the Upper Peninsula of Michigan (2B), and Northcentral Wisconsin (2C). Open circles represent LTM lakes, while dashed and dotted lines indicate percentiles of the ELS population density. (••••• 80th; —— 50th; •—• 20th; --- 5th). The smaller triangles to the right of the trilinears indicate the percent of the ELS population found in each of the subtriangles.

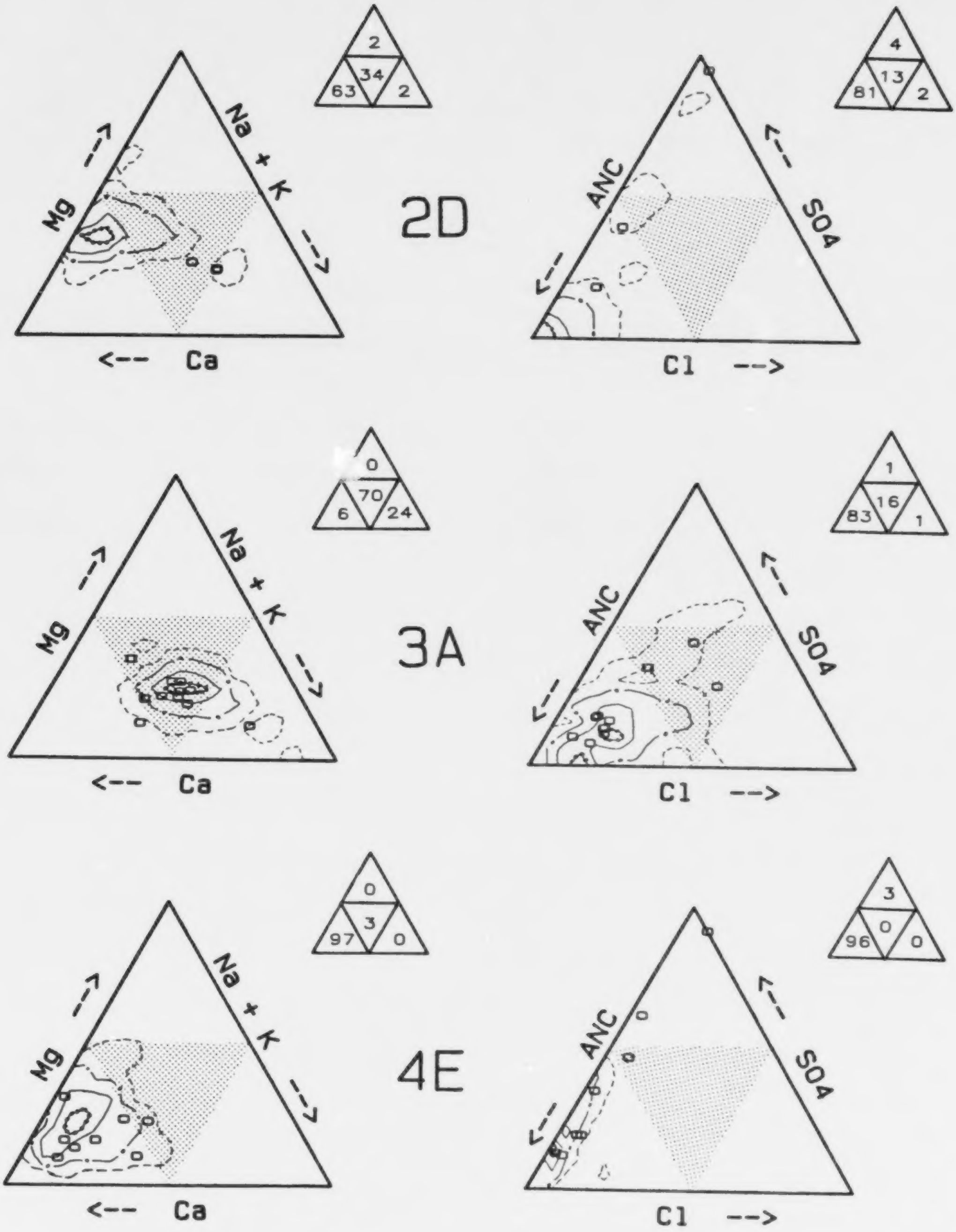


Figure 3-7. Trilinear diagrams for anions and cations for the Upper Great Lakes (2D), the Southern Appalachians (3A), and the Colorado Rockies (4E). Open circles represent LTM lakes, while dashed and dotted lines indicate percentiles of the NLS population density. (•-•-•- 80th; —— 50th; •—• 20th; – – – 5th). The smaller triangles to the right of the trilinears indicate the percent of the NLS population found in each of the subtriangles.

LTM lakes in Maine (1E) differ more from the ELS population than do LTM lakes in the Adirondacks (1A) and Central New England (1C). Maine LTM lakes are predominantly NaCl, with high, if not dominant, Cl proportions. The ELS population modes for both the anions and cations suggest a significant occurrence of $Ca(HCO_3)_2$ lakes. Although it is not possible to quantify the proportion of each lake type from these diagrams, it is clear that the positions of LTM lakes in Maine (1E) do not coincide with the ELS population modes on both the anion and cation plots. This diagram demonstrates the importance of NaCl in the ionic makeup of these systems. The Maine LTM lakes are relatively isolated from anthropogenic effects, but they are within 30 km of the coast, which explains the high salt levels.

In Northern Minnesota (2A), the LTM lakes correspond well with the ELS population modes of both cations and anions, which are carbonate systems of no particular cation dominance. LTM lakes in the Upper Peninsula of Michigan (2B) consist of both sulfate and carbonate dominated lakes, as does the ELS population, but they do not demonstrate the Ca dominance exhibited by the ELS. Rather, no cation is dominant in any of the Upper Midwest LTM lakes. LTM lakes in Northcentral Wisconsin (2C) are SO_4^{-2} dominated, as is 40% of the ELS population. Fifty percent of the ELS population is carbonate dominated, although only one LTM lake falls in this subtriangle. No cation dominance is seen in the LTM lakes, as is true for half of the ELS lakes, with the other half characterized as Ca lakes.

Only three LTM lakes were sampled in the Upper Great Lakes area (2D), and these differ from the ELS population in their Na + K dominance. Whereas 63% of the ELS population is Ca dominated and 34% is nondominated, only 2% is Na + K dominated. One LTM lake is SO_4 dominated, compared with only 4% of the ELS population.

The LTM lakes in the Southern Appalachians (3A) correspond well to the ELS population in this subregion, being carbonate dominated with a nondominated cation composition. This correspondence is reflected in the proximity of the LTM lakes to the population modes in the anion and cation trilinear diagrams.

In the Colorado Rockies (4E), most LTM lakes are $Ca(HCO_3)_2$ systems, which is also the predominant composition in the WLS population. Two LTM lakes are SO_4^{-2} dominated, and one lake has no cation dominance compared to 3% of the WLS population in each of these categories.

LTM lakes in the Adirondacks (1A), Vermont (1C), the Upper Peninsula of Michigan (2B), and Northcentral Wisconsin (2C) are well-represented by sulfate dominated lakes, whereas in the NLS, both SO_4^{-2} and HCO_3^- lakes occur in substantial proportions. As noted in Section 2.3.2, low ANC lakes were chosen for the LTM Project, while the NLS population contours reflect the entire NLS population. LTM lakes in Northern Minnesota (2A), the Southern Blue Ridge (3A), and Colorado (4E) corresponded well with the NLS populations. In general, HCO_3^- dominated in these systems; Ca was important in Colorado and no cation dominated in Minnesota or the Southern Blue Ridge. Maine LTM lakes were less like the NLS population than any other LTM lakes; they were characterized by the high sea salt influence.

3.2.3 Principal Component Analysis (PCA)

3.2.3.1 Interpretation of PCA--

PCA was used to compare LTM data to data for the ELS population, considering several variables simultaneously. PCA is a statistical method employed to explain a variance-covariance structure of several variables (m = number of variables) through a few linear combinations of the original variables, with the objectives of reducing and interpreting the data (Johnson and Wichern, 1982). These components are mutually independent and are derived in a particular order: the first accounts for the maximum possible variance in the original data (the principal axis of variation); the second component accounts for the maximum possible variance in the residual of the first; the third accounts for the maximum possible variation in the residual from the first two, and so forth for the remaining 'm' components. In practice, most of the variation is explained by the first few components. The original data cloud can then be projected in a reduced dimensional space described by the first few components. This representation reflects the percent of the original variance that is described by these components.

Each component consists of a vector of coefficients for each of the 'm' variables. Variables with large coefficients explain more variation within that component than do variables with smaller coefficients, which allows a description of each of the components in terms of the original variables. A component may be rotated in space, achieving a different set of coefficients for each variable, which may be more easily interpreted. In a successful PCA, the original data are described in terms of a few easily interpreted components, achieving the objectives of data reduction and interpretation.

3.2.3.2 Results of PCA--

PCA performed on the weighted ELS data showed that three components accounted for 75.1% of the variance. These results are presented in Table 3-3. The following items contain qualitative descriptions of the three components based on the magnitude of the coefficients:

- Component I was related to buffering capacity due to high values for conductance, Mg, Ca, ANC, Na, K, Cl^- (all positive), and H^+ (negative).
- Factor II was described as a mineral acid and salt component based on high values for Na, Cl^-, SO_4^{-2}, NO_3^-, Al, and H^+, with a negative contribution for ANC.
- Factor III was attributed to organics because of the large coefficients for DOC and color.

Positive and negative signs on the coefficients have a relative rather than an absolute meaning. Opposite signs indicate a counterbalancing effect of the coefficients.

TABLE 3-3. COEFFICIENTS FOR THE FIRST COMPONENT AND SECOND AND THIRD FACTORS RESULTING FROM THE PCA OF ELS DATA

	Component	Rotated Factors[1]	
Variable	I	II	III
Conductance	0.41	0.05	-0.02
Mg	0.40	-0.09	0.10
Ca	0.39	-0.17	0.07
ANC	0.38	-0.26	-0.06
Na	0.28	0.40	0.10
K	0.26	0.24	0.04
Cl^-	0.24	0.44	-0.17
SO_4^{-2}	0.15	0.34	-0.27
NO_3^-	0.09	0.28	0.18
DOC	0.08	-0.04	0.60
Color	0.00	0.15	0.64
Al	-0.17	0.42	0.26
H^+	-0.34	0.30	0.01
% Variance	42.1	16.5	16.5
Cumulative %	42.1	58.6	75.1

[1] These components originally accounted for 17.4 and 15.6 percent of the variance respectively, but were rotated 45° to achieve more easily interpreted factors, each accounting for 16.5% of the total variance.

Figure 3-8 contains density contour plots of the ELS population for scores of the three pairs of components I, II, and III, overlaid by a plot of the principal component scores for the LTM lakes. Unlike the trilinear contours, the percent of the ELS population within each contour has been calculated, and the density contour lines are labeled accordingly. Inspection of these plots allows the LTM lakes to be compared to the ELS population in two ways: (1) identifying any LTM lakes as obvious outliers in the population, and (2) comparing the LTM lake distributions to the ELS population distributions.

Regarding identification of LTM lakes as outliers, some LTM lakes fall into the periphery of the ELS distribution, but not outside the cluster of LTM lakes, and thus should not be considered as outliers. On a regional basis, the distribution of LTM points does not coincide with the contour rings on the plots with respect to component I, so that the distribution of the LTM lakes is characterized by lower buffering capacity than the mode of the ELS population. As indicated by factors II and III, LTM lakes do not appear different from the ELS distribution with respect to major cations, anions, and organics.

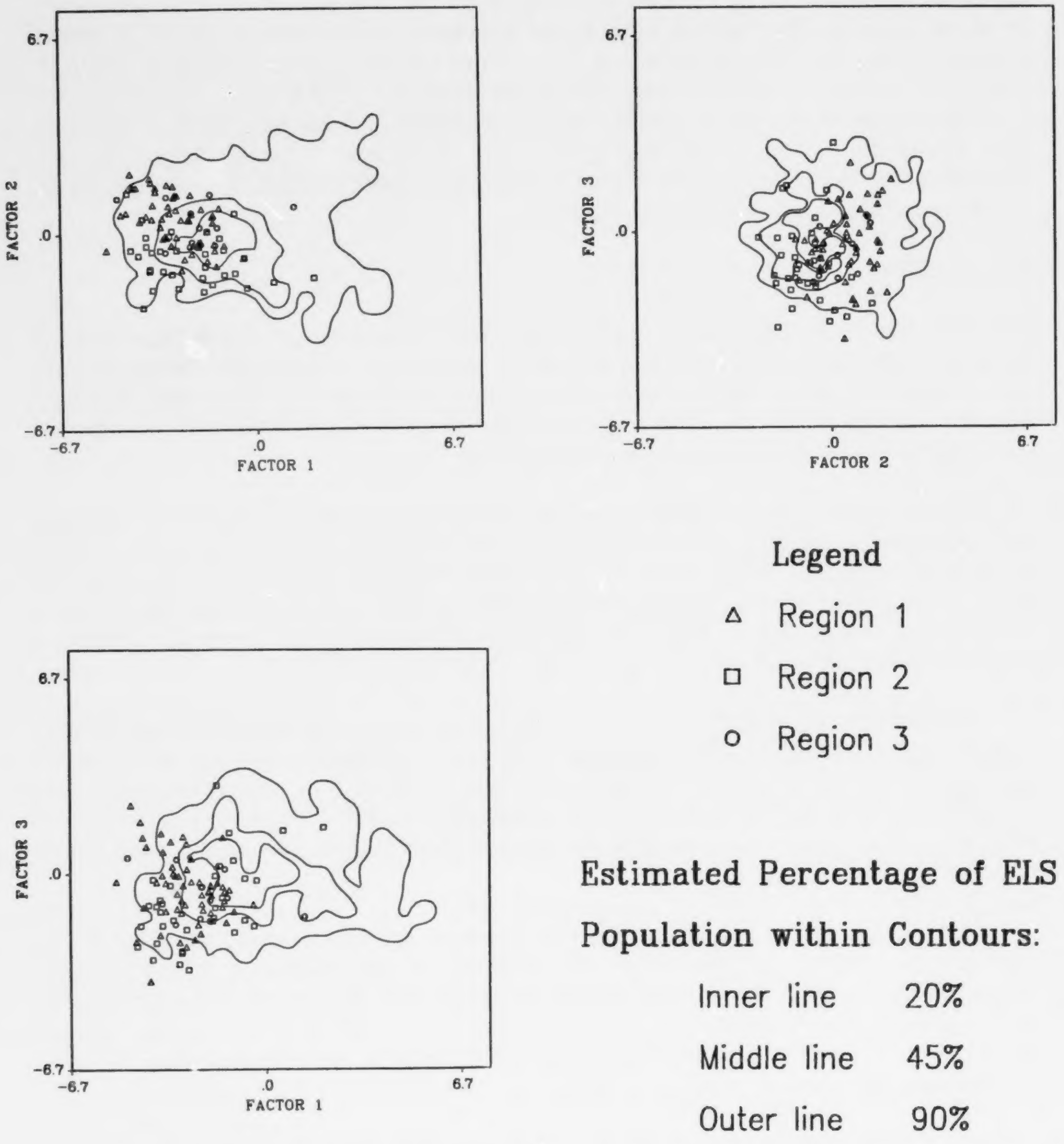
On a subregional basis however, lakes in Maine (1E) were characterized by high salt and low DOC compared to the ELS population in that subregion. In the Upper Peninsula of Michigan (2B) and Northcentral Wisconsin (2C), the LTM lakes show a disproportionate number of lakes low in organics. LTM lakes in the remaining subregions appear to have characteristics similar to those of the low ANC lakes in the ELS population.

3.2.4 Summary of LTM to NLS Comparison

LTM lakes are characterized by lower ANC values than were found in the NLS population. This finding was reflected in all three comparisons: in the F(x) curves, where most LTM lakes fell below the subregional median values; in the trilinear diagrams, which show the occurrence of so many sulfate dominated lakes; and in the PCA, in which LTM lakes had PCA scores less than zero, corresponding to the overall ELS population mean. This result is not surprising, since the LTM lakes were selected with the criterion of ANC < 200 μeq L^{-1}, which is lower than most of the NLS regional medians. Furthermore, it is desirable to include generally low ANC lakes in a monitoring program, since these lakes would be expected to exhibit the greatest changes in water chemistry in response to changing acidic deposition loadings.

Sulfate is moderately high in the LTM lakes, reflected in the F(x) curves and in the presence of so many sulfate dominated lakes. DOC in LTM lakes appears to be lower than in the NLS populations. This was indicated both in the F(x) comparisons and in the PCA. The PCA identified fewer subregions with low organic constituents than did the comparison of LTM lakes to the F(x) curves. This is likely due to use of the entire ELS data base for calculation of the principal component scores. A principal component score of zero then corresponds to the entire ELS population mean for that component. Rather than comparing LTM lakes to the subregional estimates, the PCA performed here results in a comparison of LTM lakes to the entire ELS population.

In general, the LTM lakes represent low ANC systems with a variety of other characteristics; this is desirable for a regionally representative monitoring program. However, three problems preclude the use of the LTM lakes for extrapolation to regional or subregional



Legend

△	Region 1
□	Region 2
○	Region 3

Estimated Percentage of ELS Population within Contours:

Inner line	20%
Middle line	45%
Outer line	90%

Figure 3-8. ELS population density contours of principal component scores for factor 1 versus factor 2, factor 1 versus factor 3, and factor 2 versus factor 3. LTM lakes are plotted with symbols identifying each lake's region.

characteristics. First, the lakes in the LTM program were not chosen from a defined population, so we do not know the characteristics of the population represented by the LTM sample. Second, although we could argue that the LTM sample was chosen from those lakes with ANC <200 and thus represent the population of low ANC lakes, the LTM lakes were not chosen in a way that enables us to quantify that representation. No attempt has been made to determine what proportion of the low ANC population might be represented by each lake. The third problem is that the LTM lakes are clustered within subregions and thus may not exhibit the spatial variability found across the subregion.

3.3 TRENDS

The Long-Term Monitoring Program was initiated with the intent of monitoring potentially susceptible lakes for chemical changes that might result from acidification. At present, the longest period of record available is for lakes in the Upper Midwest, where data have been recorded for seven years. The next longest data records are for Vermont and the Adirondacks, where monitoring has been conducted for four years.

Data from one lake in each of these three regions is presented in Figure 3-9. The solid line represents the overall mean ANC value; the dashed lines indicate plus or minus one standard deviation of the mean. Visual inspection of the plots shows no consistent deviation from the mean value. Only in Sucker Pond, Vermont, do the data suggest an increase in ANC. Variability in this pond is so high, however, that it is clear more data are required before a trend becomes apparent.

Data in both the Adirondacks and Vermont were sampled on consistent schedules, monthly and seasonally, respectively. For these regions, however, only four years of data are available, an even shorter period of record than that of the Upper Midwest. Any changes that might have occurred as a result of acidification are small compared to annual and seasonal fluctuations, so again it is difficult to differentiate between trends and cyclic fluctuations, from such a short record of data.

Many sites in the Upper Midwest had more complete records than Long Lake (Figure 3-9). This lake was chosen to demonstrate the difficulty of determining a change in mean concentration when so few data are available, yet variability is clearly high. Inspection of plots of the data over time showed no obvious increases or decreases of any of the primary parameters. Thus, given the above problems and the lack of any obvious trends, no trend analyses were completed.

Seven years is too short a time period to demonstrate that any changes may have resulted from acidic deposition. The estimated maximum possible decrease in ANC since the onset of increased acidic deposition at the turn of the century is about 100 μeq L^{-1} (Altshuller and Linthurst 1983). Over 80 years time, this translates to an estimated maximum acidification rate of 12.5 μeq L^{-1} ANC per decade. Within-year standard deviations for ANC range from 25 μeq L^{-1} to 245 μeq L^{-1} (see Section 3.4.3.1, Table 3-6). Despite this large within-year variability, over a time period of a decade or more, the data may display a decreasing trend. Over a shorter time period, at such a low rate of change, and with high variability, trends will not be discernible from inherent variability. The earlier data in the Upper Midwest were collected on a

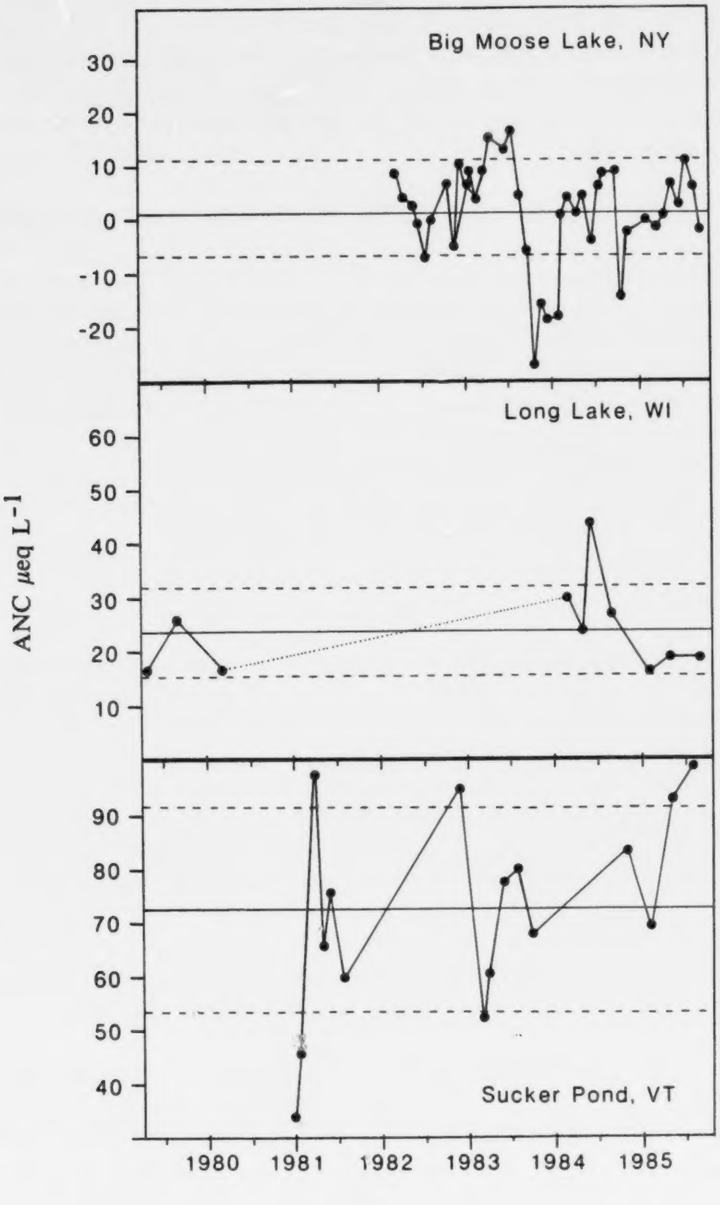


Figure 3-9. ANC in μeq L^{-1} is plotted over time for three lakes sampled during the LTM Project. (The New York and Wisconsin data include data from the RILWAS and Glass projects.) Dashed lines indicate ± one standard deviation from the mean ANC value (solid line).

sporadic schedule, sometimes in the fall and spring, sometimes quarterly, and sometimes not at all for a year or longer. As demonstrated in Section 3.4.3.1, both among-season and within-season variation is high, so that when only one sample is taken per season, and there are missing seasons, it is impossible to determine whether differences among single seasonal samples represent trends or are part of seasonal cycles. The inconsistent sampling schedule also makes it difficult to describe the autocorrelation of the data set, thus limiting the ability to detect statistically significant trends.

3.4 RESULTS OF ANALYSES OF LTM DATA AS AN AID IN PROJECT DESIGN

Even though trends cannot be detected in the LTM data, the data can be used to determine the relative importance of the different components of variability, to estimate the number of lakes that should be sampled within a region, and to describe the relationship between fall and spring chemistries. All of these analyses contribute to an understanding of inherent variability and seasonal relationships, which can be of use in optimizing a design for a monitoring program. The results of these data analyses are presented in this section. A discussion of their usefulness and limitations in program design appears in Section 4.2. In the discussion of the remaining analyses, references to LTM subregions are made by state abbreviations in order to distinguish LTM lakes from NLS lakes.

3.4.1 Regional Sample Size

LTM data were used to estimate the number of lakes to be sampled in a subregion in order to detect a specified change in the regional mean concentration of a specific variable at any given time in the future. Estimates were calculated guarding against various levels of Type I ($1-\alpha$) and Type II ($1-\beta$) errors, and for various levels of change (see Section 2.3.3). Data from the Adirondacks are presented in Table 3-4. Similar data for other subregions are included in Appendix D. Recommended sample sizes increase with increasing probability levels of $1-\alpha$ and $1-\beta$, and with decreasing levels of change. The differences in numbers of lakes to be sampled at a given confidence level within a region varies for the variable in question as a result of two things: the variability among lakes for the given parameter, and the level of change detected. Thus, for the smallest changes in ANC, pH, and SO_4^{-2}, with both $1-\alpha$ and $1-\beta$ levels of 0.95, the estimated number of lakes to be sampled in the Adirondacks varies between 66 and 217. As the level of change increases, the discrepancy among variables becomes smaller.

A comparison of the estimated number of lakes to be sampled in each LTM region at $1-\alpha$ and $1-\beta$ levels of 0.9 is shown in Table 3-5. For a given level of change here, the differences between subregions reflect regional differences in the variability of a given parameter. For instance, the estimated sample size in Subregion 1E for lakes with $20 < ANC \leq 100$ are quite small. However, only two LTM lakes fall into this category. These two lakes are characterized by a very small between-lake variability. As shown in Section 3.2, the Maine LTM lakes correspond to a small percentage of the ELS population, so LTM lake data probably underestimate subregional among-lake variability.

Comparing the estimates of the number of lakes required for detection of specified changes at various levels of significance and power to the number of lakes sampled in the current LTM project shows that increasing the number of lakes sampled in each subregion would increase the

TABLE 3-4. ESTIMATES OF THE NUMBER OF LAKES TO BE SAMPLED IN THE ADIRONDACK SUBREGION (NY) FOR VARIOUS LEVELS OF SIGNIFICANCE, POWER, AND CHANGE

		7 Lakes with ANC ≤ 20			8 Lakes with 20 < ANC ≤ 100		
		CHANGE IN ANC					
1-α[1]	1-β[2]	$10\ \mu eq\ L^{-1}$	$25\ \mu eq\ L^{-1}$	$50\ \mu eq\ L^{-1}$	$10\ \mu eq\ L^{-1}$	$25\ \mu eq\ L^{-1}$	$50\ \mu eq\ L^{-1}$
0.95	0.95	144	27	8	104	18	5
0.95	0.90	115	21	7	82	14	4
0.95	0.80	83	15	5	60	10	3
0.95	0.70	63	12	4	45	8	2
0.90	0.95	115	21	7	82	14	4
0.90	0.90	88	16	5	64	11	3
0.90	0.80	61	11	3	44	8	2
0.90	0.70	44	8	3	32	6	2
0.80	0.95	83	15	5	60	10	3
0.80	0.90	61	11	3	44	8	2
0.80	0.80	38	7	2	28	5	1
0.80	0.70	25	5	1	18	3	1
		CHANGE IN pH[3]					
1-α[1]	1-β[2]	0.2	0.35	0.5	0.2	0.35	0.5
0.95	0.95	66	21	11	52	17	9
0.95	0.90	52	17	9	41	13	7
0.95	0.80	38	12	6	30	10	5
0.95	0.70	29	9	5	23	7	4
0.90	0.95	52	17	9	41	13	7
0.90	0.90	40	13	7	32	10	5
0.90	0.80	28	9	5	22	7	4
0.90	0.70	20	6	3	16	5	3
0.80	0.95	38	12	6	30	10	5
0.80	0.90	28	9	5	22	7	4
0.80	0.80	18	6	3	14	4	2
0.80	0.70	12	4	2	9	3	2

[1] 1-α is the probability of not making a type I error.
[2] 1-β is the probability of not making a type II error (power).
[3] pH levels of change are indicated in pH units.

(Continued)

TABLE 3-4. ESTIMATES OF THE NUMBER OF LAKES TO BE SAMPLED IN THE ADIRONDACK SUBREGION (NY) FOR VARIOUS LEVELS OF SIGNIFICANCE, POWER, AND CHANGE (Continued)

		7 Lakes with ANC ≤ 20			8 Lakes with 20 < ANC ≤ 100		
		% CHANGE IN SO_4^{-2}					
1-α[1]	1-β[2]	10%	25%	50%	10%	25%	50%
0.95	0.95	217	39	12	24	4	1
0.95	0.90	172	31	9	19	3	1
0.95	0.80	125	23	7	14	3	1
0.95	0.70	95	17	5	11	2	1
0.90	0.95	172	31	9	19	3	1
0.90	0.90	133	24	7	15	3	1
0.90	0.80	91	17	5	10	2	1
0.90	0.70	66	12	4	7	1	1
0.80	0.95	125	23	7	14	3	1
0.80	0.90	91	17	5	10	2	1
0.80	0.80	58	10	3	6	1	1
0.80	0.70	38	7	2	4	1	1

[1] 1-α is the probability of not making a type I error.

[2] 1-β is the probability of not making a type II error (power).

TABLE 3-5. ESTIMATES OF THE NUMBER OF LAKES[1] TO BE SAMPLED WITHIN A REGION IN ORDER TO DETECT A GIVEN CHANGE

CHANGES IN ANC

	Number of LTM lakes in ANC class	Lakes with ANC ≤ 20			Number of LTM lakes in ANC class	Lakes with 20 < ANC ≤ 100		
		10 μeq L^{-1}	25 μeq L^{-1}	50 μeq L^{-1}		10 μeq L^{-1}	25 μeq L^{-1}	50 μeq L^{-1}
NY	7	88	16	5	8	64	11	3
VT	11	13	2	1	19	45	8	2
ME	4	34	6	2	2	5	1	1
UPMW[2]	13	73	13	4	8	78	14	4
MN	no low ANC lakes sampled				one moderate ANC lake sampled[3]			
MI	6	412	77	24	one moderate ANC lake sampled			
WI	6	20	4	1	5	30	5	2
SBR	one low ANC lake sampled				6	44	8	2

CHANGES IN pH UNITS[4]

		0.2	0.35	0.5		0.2	0.35	0.5
NY	7	40	13	7	8	32	10	5
VT	11	25	8	4	19	20	7	3
ME	4	82	27	14	2	1	1	1
UPMW[2]	13	27	9	4	8	15	5	2
MN	no low ANC lakes sampled				one moderate ANC lake sampled[3]			
MI	6	84	27	14	one moderate ANC lake sampled			
WI	6	37	12	6	5	51	17	8
SBR	one low ANC lake sampled				6	22	7	4

[1] The numbers presented in this table were calculated with an α and β level each at 0.10.

[2] The entire region includes one lake from the ELS Subregion 2D, the Upper Great Lakes.

[3] One lake is not sufficient for estimating an among-lake variance.

[4] These numbers represent a change in pH units for pH.

(Continued)

TABLE 3-5. ESTIMATES OF THE NUMBER OF LAKES[1] TO BE SAMPLED WITHIN A REGION IN ORDER TO DETECT A GIVEN CHANGE (Continued)

	% CHANGES IN SO_4^{-2}							
	Number of LTM lakes in ANC class	Lakes with ANC ≤ 20			Number of LTM lakes in ANC class	Lakes with 20 < ANC ≤ 100		
		10%	25%	50%		10%	25%	50%
NY	7	133	24	7	8	15	3	1
VT	11	30	5	2	19	22	4	1
ME	4	44	8	2	2	3	1	1
UPMW[2]	13	59	11	3	8	74	13	4
MN	no low ANC lakes sampled				one moderate ANC lake sampled[3]			
MI	6	164	30	9	one moderate ANC lake sampled			
WI	6	143	26	8	5	123	22	7
SBR	one low ANC lakes sampled				6	125	23	7

[1] The numbers presented in this table were calculated with an α and β level each at 0.10.

[2] The entire region includes one lake from the ELS Subregion 2D, the Upper Great Lakes.

[3] One lake is not sufficient for estimating an among-lake variance.

level of statistical confidence with which trends could be identified. This confidence could help prevent two errors: detecting a change when in fact there is no change (Type I error; probability of $1-\alpha$, often referred to as a significance level), and failing to detect a trend when in fact there is one present (Type II error; probability of $1-\beta$, commonly referred to as power). The most common significance level chosen for statistical inferences is 0.95, although for data collected from the environment rather than in a laboratory, many scientists believe that a significance of 0.9 is sufficient. Power is more commonly ignored, since controlling for it is more difficult. However, if a monitoring program is intended to protect resources at risk of damage, a lower significance level and a higher level of power would result in a more conservative level of protection.

For most of the eastern LTM subregions, the numbers of lakes currently sampled could result in the detection of some level of regional changes at significance and power levels of 0.9 each. For most of these, only the intermediate levels of change, 0.35 pH units, 25 μeq l^{-1} ANC, and 25% change in SO_4^{-2} concentrations would be detected. Smaller changes could only be seen with less significance and power (0.8 and 0.7) than were considered in the analyses. Vermont is the only subregion in which current sample sizes would allow detection of the smaller changes of 0.2 pH units, 10 μeq l^{-1} ANC, and 10% change in SO_4^{-2} at $1-\alpha$ and $1-\beta$ of 0.8 each.

These estimates of regional sample sizes are based on the among-lake variance present in the LTM data. As the number of lakes in each ANC class was small, and as the LTM lakes do not represent an unbiased sample from a well-defined population, these estimates of variance might not be accurate approximations of among-lake variance from a sample chosen differently.

3.4.2 Duration of Monitoring

Being able to determine how long a system should be monitored in order for a given level of change to be observed is important in planning a design for a monitoring program. Toward this end, within-lake variances were estimated for each LTM lake in the Adirondacks, Vermont, and Upper Midwest subregions. These variances were used to estimate the number of samples that will be required in the future for detecting specified levels of change at various levels of significance and power (see Section 2.3.4, equation 2).

Results of these analyses are presented as box and whisker plots (Figures 3-10 and 3-11) demonstrating the distribution of the number of years of monitoring implied for each lake. Additional data are included in Appendix E. The variances used in the calculations are based on seasonal samples. Although monthly samples were taken in the Adirondacks, median seasonal values were used to estimate this variance so that analyses from all three regions would be comparable.

The Adirondack lakes were characterized by the highest median value for the duration of monitoring required for both ANC classes in order to detect changes in ANC, pH, and SO_4^{-2}. For similar levels of change, significance, and power, this reflects higher within-lake variances in this region. The distribution of duration for SO_4^{-2} monitoring was higher for $20 < \text{ANC} \leq 100$ lakes in the Upper Midwest than for those in the Adirondacks; however, the median value for the Adirondacks exceeded that of the Upper Midwest.

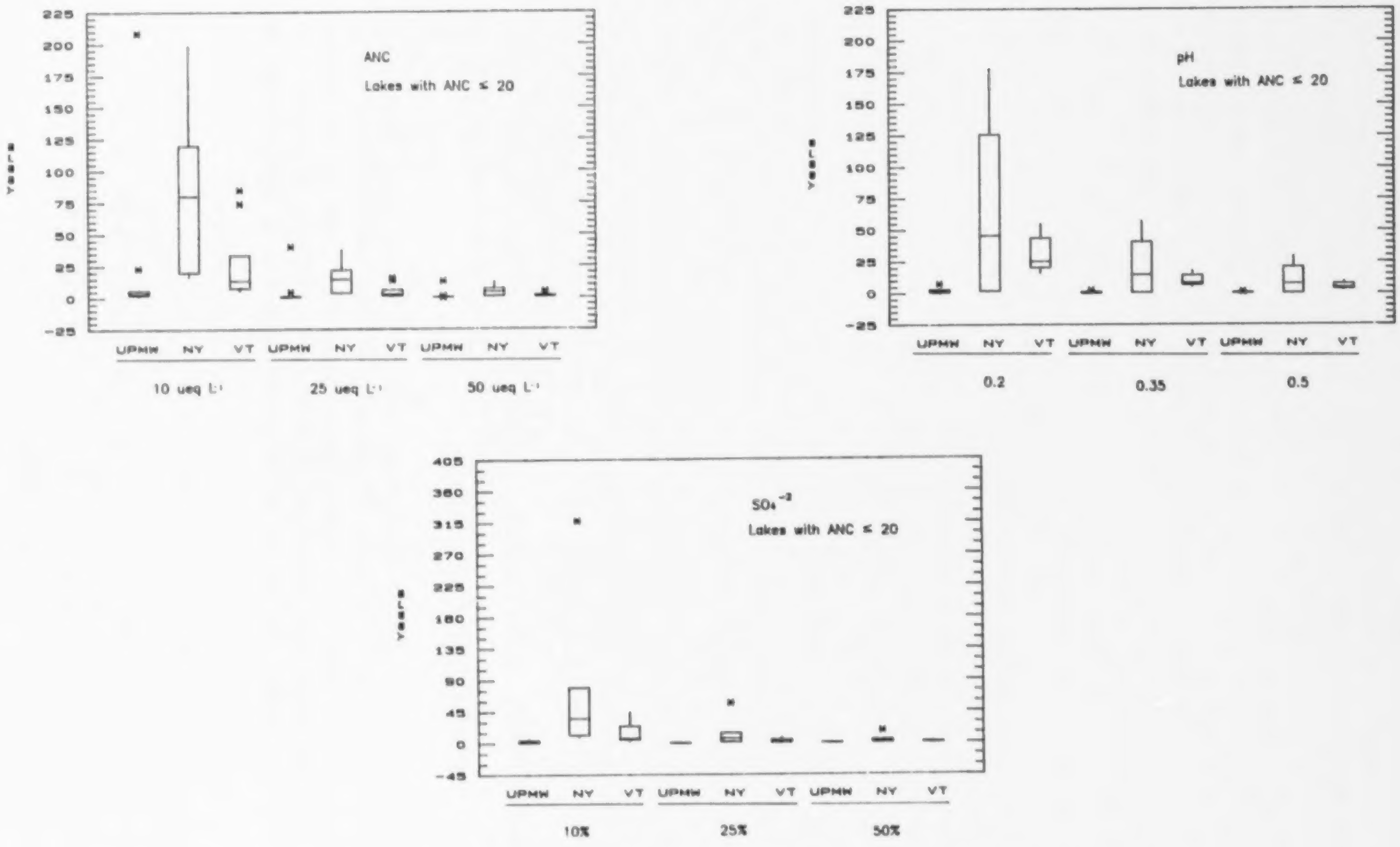


Figure 3-10. Box and whisker diagrams demonstrating the distribution of expected years of monitoring LTM lakes with ANC ≤ 20 μeq L^{-1}, in the Upper Midwest (UPMW), New York (NY), and Vermont (VT). Numbers of years to detect a 10 μeq L^{-1}, 25 μeq L^{-1}, and 50 μeq L^{-1} change in ANC, a 0.2, 0.35, and 0.5 unit change in pH, and 10, 25, and 50% change in SO_4^{-2} are shown for significance and power levels of 0.9 each.

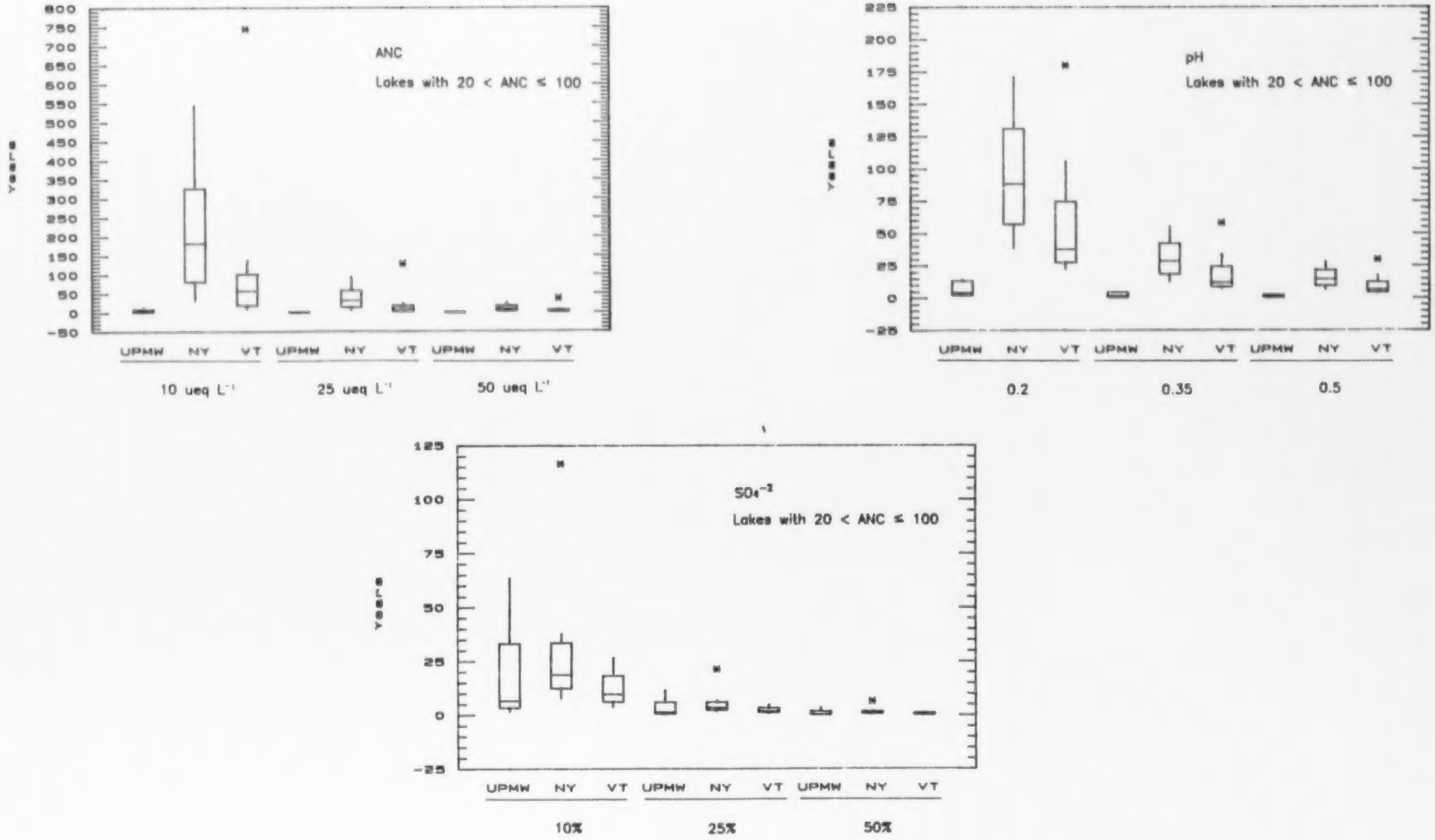


Figure 3-11. Box and whisker diagrams demonstrating the distribution of expected years of monitoring LTM lakes with 20 < ANC ≤ 100 μeq L^{-1}, in the Upper Midwest (UPMW), New York (NY), and Vermont (VT). Numbers of years to detect a 10 μeq L^{-1}, 25 μeq L^{-1}, and 50 μeq L^{-1} change in ANC, a 0.2, 0.35, and 0.5 unit change in pH, and a 10, 25, and 50% change in SO_4^{-2} are shown for significance and power levels of 0.9 each.

A major assumption of this analysis is that within-lake variance remains constant over time. Along with this assumption, the estimate for the number of samples assumes the same seasonal sampling schedule. A second major assumption is that there are no trends in the lakes monitored. The presence of an ignored trend will inflate the estimated within-lake variance. In the analyses presented here, the variance from the overall mean was calculated. If a trend were present, due to the slope of the change over time, both the early and the most recent data would deviate further from the mean, increasing the overall variance. This situation was not apparent in the LTM data. Had it been, a first differences approach (Abraham and Ledolter, 1983) would have resulted in a measure of variance about the slope. Sample sizes calculated in this way would refer to detection of a change in the trend, rather than to a change in the mean.

Interpretation of these results is somewhat confusing. The data suggest that monitoring must continue longer for detection of a small change than for a large change. However, a small change will occur before a large change does. For example, the plots indicate that half the Adirondack lakes require a monitoring duration of 90 years or more for detection of a 0.2 pH unit change, but only 28 years or more for detection of a 0.35 pH unit change. The number of samples required through time is dependent upon the within-lake variability. A small change is more difficult to detect than a large change in a system with high variability. Thus, although 90 years of monitoring at the same schedule would be required in an Adirondack lake of median variability in order to detect a 0.2 pH unit change, a larger change in pH could be detected sooner. Once a trend can be detected in the monitoring data, the analysis approach should be changed accordingly, and the estimates presented here would be adjusted.

3.4.3 Sources of Variation

Both absolute and relative measures of variability were described for the LTM data. Standard deviations give an absolute measure of variability, in the same units of measure as the parameter described. Relative variability of among-lake annual and seasonal components were calculated as percents of the total variability. These two measures describe the extent to which a given parameter may vary seasonally or annually, and the importance of the contributions of among-lake, annual, and seasonal variability.

3.4.3.1 Absolute Variability--

Seasonal and annual standard deviations are presented by subregion in Table 3-6. Among-year and within-year, and among-season and within-season standard deviations are presented. Among-year or among-season standard deviations are calculated as the standard deviation of the annual or season-within-year means. Within-year or within-season variation is the mean of the within-year or within-season standard deviations. Thus, among-year or among-season variation is an index of variation of the mean value from one year or season to the next, while within-year or within-season variation is an index of variability about each annual or seasonal mean.

Inspection of Table 3-6 shows that within-year or within-season-within-year variability is always considerably higher than among-year or among-season-within-year variability. This result indicates that there is more variability within a year than from one year to the next across the subregion. Likewise there is more variability within a season than from one season to the next,

TABLE 3-6. ANNUAL AND SEASONAL STANDARD DEVIATIONS FOR ANC, pH, AND SO_4^{-2}

	ANC $\mu eq\ L^{-1}$		[1]pH		SO_4^{-2} $\mu eq\ L^{-1}$	
	Among years	Within years	Among years	Within years	Among years	Within years
NY	6.32	64.83	0.10	0.88	4.99	26.59
VT	4.84	46.00	0.09	0.70	8.30	20.42
ME	3.20	25.87	0.09	0.70	1.24	17.82
UPMW	72.18	199.80	0.31	0.88	7.50	28.93
MN	37.11	245.09	0.13	0.56	9.24	19.48
MI	46.71	87.56	0.64	0.99	23.51	28.24
WI	8.48	14.80	0.19	0.46	10.56	31.93
SBR	40.49	101.42	0.34	0.51	5.32	23.83
	Among seasons	Within seasons	Among seasons	Within seasons	Among seasons	Within seasons
NY	14.13	63.71	0.25	0.85	7.30	26.05
VT	10.76	45.23	0.19	0.69	10.81	19.08
ME	4.79	26.97	0.12	0.74	2.42	18.92
UPMW	71.78	164.62	0.62	0.80	19.91	28.02
MN	82.77	209.29	0.57	0.49	15.15	19.14
MI	33.77	86.85	0.43	1.01	16.64	28.63
WI	8.68	14.35	0.18	0.48	10.64	30.12
SBR	28.24	117.83	0.28	0.49	5.25	26.45

[1] pH standard deviations are in standard pH units.

across a subregion. In general, among-season variation exceeded among-year variation, while within-year and within-season variations were similar. This indicates that across a region, there is greater change from one season to another than from year to year. Within-year and within-season variations were similar and greater than among-season variations, suggesting that within-season variability across a region accounted for most of the annual or seasonal variability. These results are displayed graphically in Figure 3-12. Actual ANC values, not standard deviations, were plotted across months for the Adirondack data. Boxes were then drawn around the data for each season, with the upper and lower bounds defined by the maximum and minimum value in each season. A second box was drawn around the data for each year, again with upper and lower bounds defined by the maximum and minimum values in that year. The same pattern of large within-season variation is seen, with greater differences observed among heights of the seasonal boxes than among heights of the annual boxes.

A similar figure displaying data from only one lake in the Adirondacks is also shown in Figure 3-12. This figure demonstrates that among-season variation is much greater in an individual lake than across the region. When among-lake variability is removed, it appears that both among-season and within-season variability contribute significantly to annual variability.

3.4.3.2 Relative Variability--

The standard deviations presented in the preceding section quantify seasonal and annual variation across the LTM subregional samples. The relative influences of lake, year, and season components on the variability observed in the LTM lakes may aid in the design of future programs. An analysis of variance model was used to determine the proportion of variance contributed by different factors. Table 3-7 shows the percent of the total variation from the among-lake, year, seasons-within-year, and interaction components.

Among-lake variability was always the largest single component of variability, generally accounting for more than 80% of the total variance. Exceptions to this generality were seen for ANC in Northcentral Wisconsin (WI), for pH in the Southern Appalachians (SBR), and for SO_4^{-2} in Vermont, where variation among lakes accounted for approximately half of the total variation. Correspondingly high proportions of variance were explained by the remaining effects for these variables in these subregions. When among-lake variability was low, the variability explained in the lake by season-within-year interaction term was high, indicating that in some subregions, lakes respond in a more variable way to seasonal effects than do lakes in other subregions.

Annual variability explained more of the remaining variance than did season-within-year variability for most of these subregions, with the exception of SO_4^{-2} in Vermont, where annual and seasonal variation were comparable. By adding the crossed effects, lake-by-year and lake-by-season-within-year interaction terms, the model accounted for different seasonal or annual changes occurring among lakes. Deleting these effects imposed the same annual or seasonal changes on each lake across the subregion.

3.4.4 Comparison of Spring and Fall Variability

The question of which season is most or least variable was an important consideration in developing the concept of the fall index sample for the National Lake Survey. In consideration

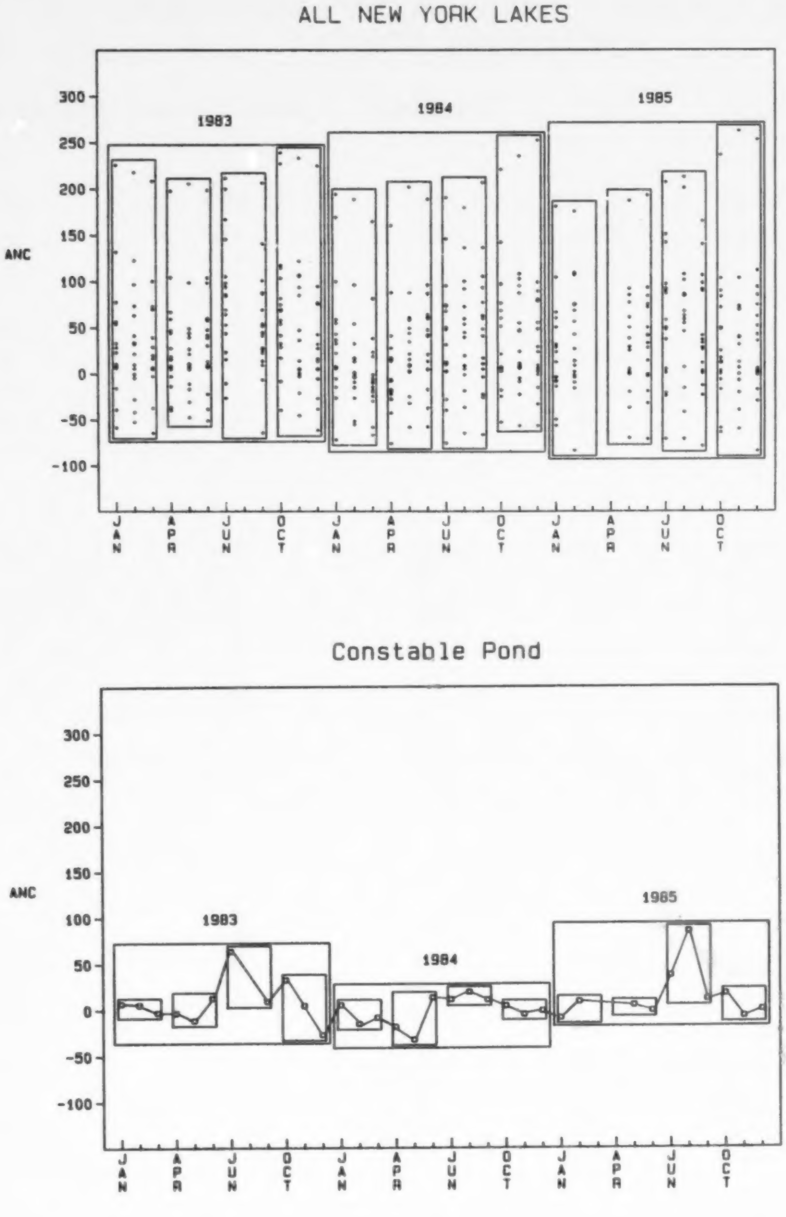


Figure 3-12. Monthly ANC values for all New York LTM lakes (top) and Constable Pond (bottom) are plotted over time. Boxes delineate maximum and minimum seasonal and annual values.

TABLE 3-7. PERCENTAGE OF VARIABILITY CONTRIBUTED BY LAKE, YEAR, AND SEASONAL EFFECTS

	Lakes	Year	Seas(Year)[1]	Lake by Year	Lake by Seas(Year)
ANC					
NY	88.39	1.08	3.93	0.98	5.63
VT	86.65	0.86	4.55	1.65	6.29
ME	92.36	1.09	2.10	2.07	2.39
UPMW	89.70	5.12	2.02	0.35	2.80
MN	83.00	2.43	2.74	6.82	5.01
MI	90.59	1.99	1.30	1.61	4.51
WI	57.95	19.49	7.92	3.98	10.66
SBR	95.07	3.66	0.64	0	1.43
pH					
NY	86.93	1.44	6.36	0.95	4.34
VT	86.66	1.16	4.96	1.15	6.07
ME	96.30	1.23	1.35	0.38	0.74
UPMW	93.80	5.62	4.86	0	0
MN	72.98	2.69	7.86	3.93	12.54
MI	98.10	2.08	0.23	0	1.04
WI	77.39	8.85	3.18	4.72	5.86
SBR	45.00	15.57	4.07	14.75	20.62
SO_4^{-2}					
NY	82.16	1.29	6.00	3.54	7.01
VT	57.54	10.69	12.39	6.56	12.83
ME	96.26	0.35	1.37	1.04	0.97
UPMW	87.49	3.51	2.46	4.87	1.67
MN	69.48	15.45	4.21	7.67	3.18
MI	91.89	4.42	1.75	0.71	1.24
WI	86.78	10.03	1.46	0	3.66
SBR	93.56	1.15	1.70	1.58	2.01

[1] Seas(Year) refers to a nested effect of season within each year.

of this problem, two sources of variability were important: within-lake and among-lake. A single annual sample was to be collected at a time when the sample would optimally represent the entire water column, and when within-lake variability would be low. LTM data cannot be used for assessments of within-lake variability, because single samples were collected monthly or seasonally, and thus cannot describe temporal or small-scale spatial variability. In order to compare data both within a region and among regions, a single sample should be collected from lakes under similar conditions (i.e., low among-lake variability). As LTM data was collected seasonally, it can be used to estimate this variability.

Inspection of Figure 3-12 (page 57) shows that across the Adirondack LTM lakes, the winter season is the least variable, suggesting that winter might be the best time to sample, since among-lake variability would be lowest. However, because monthly data were not collected in other subregions, this analysis has not been completed for them. Winter may not be the least variable season across all subregions. Also, ice-covered lakes are usually stratified, while ice-free lakes are often well-mixed under winter conditions. Thus, while among-lake variability within a subregion may be low, among-lake variability across regions may be high, due to the presence or absence of ice cover. Summer appeared to have the highest among-lake variability in the Adirondacks. Lakes are generally stratified in summer, and below ice cover in winter, so a single sample in either season would be unlikely to represent the entire lake. Dimictic lakes are generally unstratified in the spring and fall; thus, these seasons should be evaluated for within-lake variability characteristics.

Among-lake variability was compared for spring and fall data from the LTM lakes. No significant differences were found in among-lake variability between fall and spring for any of the LTM subregions. In most years, fall variability exceeded spring variability of ANC in all subregions, with the exception of Northcentral Wisconsin (WI), where spring variability exceeded fall variability, again not significantly. Sample sizes of both numbers of lakes and numbers of years are small in the LTM data set, so the appearance of such a trend may not be meaningful. However, this trend, although not significant, suggests that among-lake variability may be slightly higher in fall than in spring.

Within-lake variability could not be estimated from the LTM data due to the sparse sampling schedule and the single sampling site per lake. However, within-lake variability is important in determining the optimal season for an index sample. Results of such a study may help characterize the differences between spring and fall variability.

3.4.5 Fall Index

Spring-to-fall relationships were examined for the primary variables ANC, pH, SO_4^{-2}, and Ca. In the NLS (Linthurst et al. 1986; Landers et al. 1987), lakes were sampled in the fall under the assumption that fall samples would in some way represent lake chemistry throughout the year. If a fall index sample can indeed be used to estimate lake chemistry in other seasons, then it may be beneficial to design a monitoring program in which some lakes are sampled once a year and others are sampled more intensively.

Results of the relationships between fall and spring values for ANC, pH, SO_4^{-2}, and Ca are shown in Table 3-8. Most of the coefficients of multiple determination (R^2) are high, with

TABLE 3-8. CHARACTERISTICS FOR SPRING-TO-FALL RELATIONSHIPS OF ANC, pH, SO_4^{-2}, AND Ca (Equation 4, Section 2).

	ANC				pH				SO_4^{-2}				Ca			
	R^2	n	Slope	IV	R^2	n	Slope	IV	R^2	n	Slope	IV	R^2	n	Slope	IV
NY	0.90	66	$m < 1$	yr	0.92	64	$m = 1$	yr	0.83	66	$m < 1$	yr	0.91	66	$m < 1$	yr
VT	0.85	91	$m < 1$		0.79	89	$m < 1$	yr	0.55	90	$m < 1$	yr	0.93	89	a	yr
ME	0.97	12	$m < 1$		0.95	12	$m = 1$		0.97	11	$m > 1$		0.89	12	$m = 1$	
MN	0.88	15	$m < 1$	yr	0.88	23	$m = 1$		0.90	23	$m = 1$	yr	0.92	23	$m = 1$	yr
MI	0.97	32	$m < 1$	yr	0.97	36	$m < 1$	yr	0.96	36	$m < 1$	yr	0.98	35	c	yr
WI	0.54	27	$m = 1$		0.87	29	$m < 1$	yr	0.84	26	$m = 1$		0.98	28	$m > 1$	yr
SBR	0.95	23	$m = 1$		0.17[d]	23	$m < 1$		0.88	23	$m = 1$		0.97	22	$m = 1$	

Legend:

R^2 is the coefficient of determination for the model.
n is the sample size used in the model.
IV is the indicator variable used in the model.
m is the slope as determined by the model.

[a] slope not different from 1 for one year and less than 1 for all others.
[b] slope varies from < 1 to > 1 across years.
[c] slope > 1 two out of three years, and not different from 1 in the remaining year.
[d] $p = 0.292$

values of 0.8 or higher. Notable exceptions to this are the values for ANC in Northcentral Wisconsin (WI), pH in the Southern Blue Ridge (SBR), and SO_4^{-2} in Vermont (VT). The very low correlation between spring and fall pH in the Southern Appalachians (0.13) had a significance level of 0.054. The other two relationships, somewhat weak with R^2 values of 0.45 and 0.52, were both highly significant, with $p = 0.0001$, the low R^2 describing greater scatter than that observed in other subregions.

The slopes for most subregions for all variables were equal to or less than one, indicating that spring values either were not different or were lower than fall values. Slopes significantly greater than one were found for SO_4^{-2} in Vermont (VT) and Ca in Northcentral Wisconsin (WI). This indicates that spring SO_4^{-2} and Ca concentrations are generally higher than fall concentrations for the LTM lakes in these regions. Spring values for ANC were generally lower than fall values except in Northcentral Wisconsin (WI) and the Southern Blue Ridge (SBR), where spring and fall ANC values were comparable. This corresponds to the higher spring Ca concentrations seen in Northcentral Wisconsin (WI) as well. Spring and fall pH values were comparable in the Adirondack (NY), Maine (ME), and Northeastern Minnesota (MN) LTM lakes. In the remaining LTM subregions, spring pH values were lower than fall values. Spring and fall values of SO_4^{-2} were equal only in Northeastern Minnesota (MN); spring SO_4^{-2} concentrations exceeded fall concentrations in the Maine LTM lakes. In other regions, SO_4^{-2} concentrations were lower in spring than in fall.

The generally lower ANC values observed for spring samples in northern subregions were probably associated with the snowmelt phenomenon (Driscoll and Schafran 1984; Jeffries et al. 1979). Snowmelt has been linked with short-term depressions in ANC and pH, as well as with an increased mobilization of aluminum. Lowered spring values were observed to be less pronounced for pH than for ANC. The generally lower spring values for SO_4^{-2} (all subregions except Maine) were consistent with a dilution effect, which has been documented for the latter phases of snowmelt (Keller 1983; Sullivan et al. 1986). The extent to which dilution, SO_4^{-2}, NO_3^-, Cl^- from sea spray, and organic acids are involved in spring ANC depressions is not known. Extensive data on episodic events, including lake, soil water, snow melt, and deposition chemistries, over the duration of the spring episodes would be required to determine the cause of these observations.

For each of the variables investigated, spring-to-fall relationships differed across years in some subregions. This is not surprising, since we might expect these parameters to vary from year to year. Despite the strong relationships demonstrated between spring and fall, the analysis completed here has not determined how well the fall data reflect spring chemistry. When spring-to-fall relationships are parallel from one year to the next, differing only in the y-intercept term, then fall values are low in years when spring values are low. When this is true, fall values alone may be used to follow long-term trends. However, if the slopes differ among years, as they do for Ca in Vermont (VT) and Michigan (MI), then trends seen among fall values will not reflect the trends occurring among spring values. Although most relationships described here indicate that parallel slopes were present when year was a significant covariate, only a few years of data were available for analysis. These years occurred in succession over a short time period, thus the data at hand may not reflect the range of relationships that occur over a long time period.

3.4.6 Summary

Regional sample size estimates indicated that increasing the number of lakes sampled in a region would increase statistical confidence in characterizing regional trends, given the among-lake variability of the current LTM lakes. The lakes monitored in the current LTM program demonstrate a wide range of within-lake variability, which means that monitoring may be required over a long time period in some lakes before changes in water chemistry are detected. Analysis of variation demonstrated that among-lake variability is by far the largest component of variability, followed by within-season variability. These findings indicate that increasing the number of lakes sampled and the number of samples collected per season could result in an increased ability to detect regional changes.

Spring and fall among-lake variations were comparable in the LTM data. Fall samples also were shown to correlate with spring chemistry, demonstrating that a fall index sample, combined with intensive monitoring to complement the fall index calibration, is a reasonable approach for a monitoring project design.

3.5 THE IMPORTANCE OF METEOROLOGICAL DATA

Meteorological events influence lake hydrology and thus may explain a significant amount of among-lake or within-lake variability or they may be highly correlated with other seasonal effects and fail to explain additional variation. A general linear model composed of independent variables for year, season, and meteorological data was developed to determine if meteorological data accounted for significant variability (see Section 2.3.7).

Results from the general linear model used to assess the contribution of meteorological data to an understanding of chemical parameters are presented in Table 3-9. The percentages of within-lake variability explained by precipitation, average temperature, and annual and seasonal effects are presented. The relative contribution of precipitation or temperature to the model was not consistent among variables within a subregion nor among subregions for a particular variable.

Table 3-9 also indicates the effect that addition of the meteorological parameters has on the autocorrelation present in the model. Autocorrelation of residuals can indicate two things. In data taken over time, it demonstrates that a result at one point in time is influenced by prior events. This type of autocorrelation is called serial correlation. Autocorrelation may occur in linear models, without serial correlation, and indicates that the X values of a model are not independent. The presence of either type of autocorrelation shows that the model is ill-fitting. Autocorrelation was assessed for these models, since the data were collected over time.

For the LTM Adirondack data, inclusion of precipitation and temperature data in the general linear model decreased autocorrelation present for SO_4^{-2} and Ca. A similar result was seen for ANC in the Upper Peninsula of Michigan (MI) and for SO_4^{-2} in Northcentral Wisconsin (WI). Inclusion of precipitation and temperature data in the Vermont (VT) models failed to significantly improve the fit of the model for all four parameters. Autocorrelation was actually increased slightly for ANC, pH, and SO_4^{-2} in Vermont, as well as for Ca in Northcentral Wisconsin (WI) and for pH in the Adirondacks (NY), when the meteorological parameters were

TABLE 3-9. PERCENT OF WITHIN-LAKE VARIABILITY EXPLAINED BY PRECIPITATION, TEMPERATURE, YEAR, AND SEASON-WITHIN-YEAR EFFECTS

		ANC	pH	SO_4^{-2}	Ca
NY	precipitation	25	20	0	55
	temperature	23	36	24	8
	year	42	40	68	19
	season-within-year	10	4	8	18
	autocorrelation[1]	D	I	D*	D*
VT	precipitation	8	8	10	8
	temperature	21	26	8	13
	year	28	22	66	40
	season-within-year	43	44	16	39
	autocorrelation[1]	I	I	I	D
MN	precipitation	23	19	14	23
	temperature	19	26	6	5
	year	44	9	47	69
	season-within-year	14	46	32	2
	autocorrelation[1]	NC	D	NC	NC
MI	precipitation	51	39	18	34
	temperature	9	12	16	8
	year	18	40	50	51
	season-within-year	22	8	15	6
	autocorrelation[1]	D*	D	NC	D
WI	precipitation	46	7	10	20
	temperature	22	45	26	30
	year	16	27	59	40
	season-within-year	16	22	4	10
	autocorrelation[1]	D	D	D*	I

[1] D indicates that autocorrelation decreased with addition of meteorological parameters.

D* indicates that autocorrelation was decreased from a significant (0.05) to a nonsignificant level.

I indicates that autocorrelation increased.

NC indicates that no change occurred in autocorrelation with addition of precipitation and temperature.

added. In all these cases, however, the increase in autocorrelation was slight, and never resulted in creating a significant correlation from a previously nonsignificant correlation.

The NOAA data included in these models represent only a rough estimate of the meteorological effects on any given lake, since only monthly data were available from sites that were sometimes distant from at least some of the lakes. These results indicate however, that more accurate data may help considerably in building models to analyze time trends in some of the important chemical parameters affected by acidification.

SECTION 4

IMPLICATIONS FOR FUTURE PROGRAMS

4.1 RECOMMENDATIONS FOR QUALITY ASSURANCE AND QUALITY CONTROL

Since quality assurance and quality control (QA/QC) are important aspects of any program involving data collection, a program designed to monitor changes over time must ensure that the data are collected with a known, high level of accuracy and precision. Higher levels of analytical precision mean that there will be less variability in the data, which then decreases the overall variability and increases the likelihood that statistically significant changes can be detected. QA/QC data in the LTM Project were not adequate for estimating precision or accuracy with confidence.

The available audit data, indicating a relative overall bias of 0.3 % ± 38.4 (Section 3.1), were too variable to estimate between-laboratory bias. Blank and duplicate data were too scanty to obtain good estimates either of possible contamination or of precision (Section 3.1). A more rigorous QA/QC program could identify and quantify inter-laboratory bias, and would enable smaller confidence bounds to be placed about the data collected. Such a program should require an increased number of blank and duplicate samples and include periodic analyses of stable audit samples so that inter-laboratory bias could be assessed. LTM cooperators complied with EPA guidelines for numbers of blanks and duplicate samples. The guidelines are based on percentages of the total number of samples, with no minimum criteria. Future QA/QC designs should include minimum numbers of blank and duplicate samples, so that the number of samples collected will be large enough to permit estimates of precision with confidence. To insure that accuracy is maintained over time, an audit system should be designed that is capable of detecting changes in bias from one year to the next, as well as detecting bias among laboratories at any point in time.

The main objective of a long-term monitoring program is to assess rates of change within selected lakes. Although rates of change among regions may be compared, direct comparison of data from different regions will not be necessary, which means that no need for a centralized laboratory is implied. But the use of several laboratories adds another source of variability to the data, making it difficult to compare changes among regions. If a large number of analyses requires the use of more than one analytical laboratory, however, the data will be more comparable if all analyses for a given region are completed by the same laboratory. In this case, a protocol must be designed and maintained to ensure that samples for a given region are analyzed by the same laboratory over time and that a rigorous QA/QC program is followed by all laboratories. This protocol should include guidelines for (1) the preparation of audit sample material, (2) the collection of duplicate and replicate samples, and (3) the procedures for minimizing the impact of program changes in sampling, analytical procedures, and analytical laboratories.

Data management has been a major problem with the current LTM data (Section 2.2.1). The unique data reporting methods and the differences in parameters measured among regions have created an extremely difficult data management task. It is essential that this operation be streamlined in order to create and maintain a user-friendly, error free data base. A protocol for reporting data should be developed that is appropriate for each region independently, as well as for all regions collectively. Although parameters of interest may differ slightly among regions, the major goals of the program will be common to all regions. Thus the same analyses will be performed and compared among regions. For this reason, data management for all regions should be identical.

4.2 SAMPLING DESIGN FOR A FUTURE LONG-TERM MONITORING PROGRAM

The lakes chosen for the current Long-Term Monitoring Program are low ANC lakes that encompass a broad cross section of lake chemistry. For example, lakes may have varying DOC concentrations or anion and cation balances. This variety in classes of lakes potentially sensitive to acidification is a desirable feature for two reasons. First, if lakes of differing chemistry change in different ways, the changes may still be detected because lakes with differing characteristics are included in the population of monitored lakes. Second, long-term monitoring of such a diverse population may lead to an understanding of the processes involved in acidification, and thus allow us to better predict the impacts of acidification.

Despite the cross section of chemical characteristics found in the current LTM program, extrapolation to a regional characterization has not been completed because the lakes were not selected from a well-defined population. To correct this in any future programs where regional characterization is desired, the selection criteria should be rigorously defined, the population identified, and the selection of particular lakes done in a manner that will allow a quantification of the subregional representation of each lake. In future programs, this should include physical criteria, such as hydrologic type, bathymetry, and surrounding watershed characteristics, in addition to chemical parameters. Without a rigorous selection procedure, monitored lakes may provide useful information, but inferences about the subregion may not be accurate.

The analyses presented in Section 3 provide some guidelines for designing a monitoring program. A major factor in planning is that the largest single variability component was due to among-lake variability. Thus, if the primary objective of monitoring is to assess regional chemistry, then a large number of lakes across a region should be sampled. Within-lake variability is often high as well, however. If a primary objective of monitoring is to characterize within-lake trends, then a large number of samples must be taken within a small number of lakes over time. Tracking within-lake trends across a region then requires a sampling design that would optimize both these objectives. The LTM data have been used to estimate sampling sizes for the two separate objectives by estimating the number of lakes that should be sampled regionally and the number of samples that should be taken through time on a seasonal schedule. These estimates are based on the current LTM sites, which may not comprise an unbiased or known proportion of low ANC lakes. In addition, the small numbers of LTM lakes may have led to inaccurate estimates of among-lake variance, which were used in estimating subregional sample sizes. The data presented in this report thus should be used only as a guideline.

A comparison of spring and fall among-lake variability demonstrated no significant differences between the seasons, indicating that either season may be an appropriate time for collection of a regional index sample. LTM data could not be used to investigate within-lake variability, however, which is another crucial component to be considered in a sampling design. Two important concerns that must be addressed by analysis of within-lake variance are (1) spring and fall comparisons of within-lake spatial variability and (2) the duration of the period of mixing. Further analysis is thus required to determine the optimal season for collection of index samples.

Spring-to-fall comparisons demonstrated strong linear relationships between the seasons. These relationships were found to differ among subregions and years. Also, the relationships were not always parallel from year to year, indicating that careful calibration is required on a subregional, annual basis, if the index concept is adopted as part of a monitoring program.

For these reasons, a sampling design should be considered that includes (1) seasonal sampling every year for a carefully chosen subset of lakes and (2) occasional seasonal sampling (such as every 5 years) of all lakes, in order to confirm the accuracy of the model. This approach would help to ensure an accurate characterization of regional chemistry through time in a sampling design that provides for a large number of lakes to be sampled annually and a smaller number to be sampled more often throughout the year.

Data from the LTM project have been used here to identify some critical guidelines for development of a more rigorous monitoring program. QA/QC guidelines should be standardized among all cooperators and designed in a way that will assure that data taken over time will be comparable. The lakes sampled for such a program should consist of a well-characterized sample from a well-defined population. Analyses from the current project indicate that sampling a larger number of lakes in each subregion will allow regional changes to be identified with greater confidence. The data also suggest that monitoring must continue over a long time period to allow the detection of trends that may be related to acidic deposition, as within-lake variability is often high and the rates of change caused by deposition are expected to be low. Cursory analysis of meteorological data suggest that some measure of precipitation and temperature account for significant variability. It is likely that more accurate meteorologic and hydrologic data will explain an even greater percentage of variability. Regional seasonal relationships indicate that a monitoring design combining annual sampling of a large number of lakes with intensive sampling of a smaller number of regionally characteristic lakes is feasible. However, the among-lake and within-lake variability demonstrated in the LTM data suggests that the details of such a design should be scrutinized before implementation. Otherwise, the small changes in lake chemistry expected to result from acidic deposition rates may be indistinguishable from the inherent variability.

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SECTION 5
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APPENDIX A

WORKING PROTOCOL FOR SAMPLING, SAMPLE ANALYSIS, AND QA/QC FOR THE USEPA LONG-TERM SURFACE WATER MONITORING PROGRAM

Introduction

An EPA program for long-term monitoring of lakes and streams was initiated in 1982 within the NAPAP organizational framework. An ad hoc committee, with representation from USEPA, USGS, TVA, USD-FS, USFWS, USNPS, and Brookhaven National Laboratory, developed a draft sampling and analysis protocol to standardize monitoring efforts among the member Task Group E agencies. This document, with periodic reviews and updates, has served as the standard protocol for the EPA surface water monitoring program since its inception.

In 1984, EPA initiated the National Surface Water Survey (NSWS). This three-phase program is scheduled to culminate in the selection of geographically representative lakes for long-term monitoring in the east, upper midwest, and mountainous west. This third phase of NSWS is expected to subsume the existing long-term monitoring program. Most of the existing sites are probably compatible with Phase III owing to their location in low alkalinity regions and their positioning with respect to minimization of extraneous effects that could compromise interpretations of observed changes or trends.

The methods manual developed for NSWS (Hillman et al.) has been used, together with the Task Group E sampling and analysis protocol document, to produce the present "working protocol" for the long-term monitoring program. Laboratory analytical methodology, detection limits, and QA/QC procedures are more adequately and precisely specified; site selection criteria are not included. The objective has been to align the long-term monitoring methodology with that of NSWS, without undue disruption of existing monitoring procedures. The present document replaces the Task Group E protocol (Aquatic Effects Task Group, March 1984 revised) as the procedural document for the EPA monitoring program. Participating agencies and institutions must be able to demonstrate their use of these or equivalent sampling, analysis, and QA/QC procedures. Audits will be conducted to determine compliance with these procedures.

This document recognizes that U.S. Geological Survey protocols used in their stream research and monitoring program are not necessarily identical with those set forth here. By prior agreement with the EPA project officer, USGS protocols are acceptable in the existing cooperative EPA-USGS stream studies. Differences are few, and are noted where appropriate in this document. The USGS laboratory at Denver, where samples from the cooperative studies are analyzed, is a participant in the NSWS. Therefore, there should be no differences in laboratory analytical methodology.

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1.0 COLLECTION OF SAMPLES IN THE FIELD

1.1 Lakes

Lakes should be sampled near their deepest points (at least 20 m from shore if possible). If the water column is not thermally stratified, one sample should be collected approximately one-half meter beneath the water surface. If the water body is stratified, one sample should be collected approximately one-half meter beneath the water surface and a second one or two meters above bottom. These two samples should not be mixed or composited. A plastic closing sampling device of the Van Dorn type should be used to obtain samples at depth; do not use a metal sampler. Samples should be collected from the sampling device in plastic bottles that have been treated as described in 3.0. (See 6.1 regarding replicate samples).

1.2 Streams

Samples are obtained by hand as near mid-stream as possible, using a properly cleaned and rinsed plastic container of appropriate size. (See 6.1 regarding replicate samples). Keep hand away from mouth of container, and minimize the number of persons handling samples.

1.3 Carefully record any observed conditions that might affect analysis or interpretation of samples in field notes or sampling log.

1.4 Key project personnel who are responsible for sample integrity must be identified.

2.0 MEASUREMENTS

A set of "core" measurements are specified for the EPA monitoring program. These measurements, which are considered to provide sufficient characterization of stream or lake water quality for assessment of sensitivity and changes related to acidification, are:

pH (field and laboratory air-equilibrated)
total alkalinity
specific conductance
temperature
Secchi disc transparency (lakes)
true color
major cations (Ca, Mg, Na, K)

major anions (SO_4, NO_3, Cl)
total aluminum (filtered)

Additional measurements, including titrated acidity, DIC, DOC, F^-, Fe, Mn, NH_4, SiO_2, and total P, are being made by NSWS; some of these analyses, while not required, are also being made by some cooperators in the monitoring program.

Care must be taken to assure that the highest quality deionized water is used throughout all stages of sampling and analysis. Specific conductance of such water should not exceed 1.0 µS/cm.

3.0 SAMPLE CONTAINERS

3.1 Type

Containers should be composed of high density linear polyethylene, with polypropylene caps (do not use polyseal caps).

3.2 Cleaning of Plastic Containers

3.2.1 Containers to be used for pH, acidity, alkalinity, and anion determinations will be rinsed three times with deionized water, filled with deionized water and allowed to stand for 48 hours, then emptied and sealed in clean plastic bags until used in the field.

3.2.2 Sample containers for cations and metals will be rinsed three times with deionized water, rinsed three times with 3N HNO_3 (prepared from Baker Instra-Analyzed HNO_3 or equivalent), then rinsed six times with deionized water. They will then be filled with deionized water and allowed to stand for 48 hours. They are then emptied, capped, and placed in clean plastic bags.

3.2.3 After the initial cleaning, 5 percent of the containers will be checked by filling with deionized water, capping, and slowly rotating the container so water touches all surfaces. Check conductivity; if greater than 1 µS/cm in any of the checked containers, rerinse all containers and retest 5 percent.

4.0 SAMPLE FILTRATION

4.1 For anion analysis (including SO_4, NO_3, Cl): Rinse a cleaned 250 ml bottle three times with sample water which has been filtered directly into the sample bottle (discarding each rinse). Then fill to 250 ml with filtered sample. Use a 0.45 μm pore size membrane filter (e.g., Nucleopore polycarbonate or cellulose acetate). Ice or refrigerate. A good portable unit for filtering samples at field sites is described by Kennedy et al., 1976.

4.2 For metals and cation analyses (including Ca, Mg, Na, K): Filter 100 ml of sample into an acid-washed bottle (see 3.2.2) after rinsing three times by passing 100 ml of sample through a 0.45 μm filter and discarding each rinse. Add a 1-ml ampoule of concentrated ultrapure nitric acid (Baker Ultrex or equivalent) to the sample. Ice or refrigerate.

4.2.1 U.S. Geological Survey presently uses 0.1 μm filters for Al, Fe, and Mn in their stream work. (They are conducting comparisons of various pore sizes).

4.3 Samples for pH, alkalinity, specific conductance, and true color are not filtered.

5.0 SAMPLE PRESERVATION AND MAXIMUM HOLDING TIMES

5.1 Refrigeration at 4°C is the only recommended method of preservation for the following constituents. (Maximum allowable holding times appear in parentheses). For present purposes, icing must be considered equivalent to 4°C refrigeration.

specific conductance (14 days)
color (48 hr)
pH (no approved holding time; field sample should be analyzed immediately, and air-equilibrated laboratory samples as soon as possible)
alkalinity (14 days, according to NSWS protocol)
sulfate (28 days)
chloride (28 days)
silica (28 days)
nitrate-nitrogen (7 days)

5.2 Refrigeration at 4°C plus acidification with nitric acid to pH < 2 is recommended for the following constituents:

calcium (6 months)
magnesium (6 months)
sodium (6 months)
potassium (6 months)
aluminum (6 months)

5.3 Labels on all containers should include sufficient information to permit tracing the sample back to point and time of collection.

6.0 QA/QC SAMPLES: LAKES

Replicate samples, filtration blanks, and container blanks (total of four additional samples) are to be obtained one time for approximately every ten lakes sampled, as described below in Sections 6.1, 6.2, and 6.3. These are minimum requirements. For each project, this results in the following:

	No. of Rep/Blank Sets	
Project	Per Sampling Interval*	Per Year
University of Minnesota	3 (1/state)	9
University of Maine	1	3
Vermont	2	8
Syracuse University	2	8
TVA	1	4
USGS Colorado	2	6

[*] Sampling intervals are:
Minnesota, Maine -- spring, summer, fall.
Vermont, TVA -- spring, summer, fall, winter.
Syracuse -- quarterly (17 lakes are sampled monthly; 2 rep/blank sets per quarter).
Colorado -- monthly, summer only.

6.1 Replicate Samples

Obtain a replicate sample by repeating step 1.1 or 1.2. These replicate samples are analyzed to determine the adequacy of the sampling process in obtaining a representative sample of the lake or stream at a particular point in time.

6.2 Filtration Blanks

Prepare two filtration blanks by filtration of deionized water into properly cleaned (1) anion container (3.2.1) and (2) cation container (3.2.2). Analysis of the filtrate for the appropriate ions determines the adequacy of the filtration process and the cleanliness of the sample containers.

6.3 Container Blanks

Prepare one unfiltered container blank by filling a properly cleaned container (see 3.2.1) with deionized water. Analysis of this sample for pH, alkalinity, specific conductance, and strong/weak acidity (if applicable) provides a check on the adequacy of the container.

6.4 EPA-USGS Cooperative Stream Monitoring Projects

Replicate samples, filtration blanks, and container blanks will be taken at the primary (intensive) stream site each time that site is sampled. In addition, replicates will be obtained on two satellite streams three times yearly under low, intermediate, and high flow conditions.

7.0 MEASUREMENT METHODS

7.1 pH

7.1.1 Field measurement. Measure as soon after collection as possible. pH should be measured to ± 0.02 units using a high quality pH meter with an expanded or digital scale. A good electrode is the Corning No. 476182 glass combination or the Ross Model 81-02. The electrode should be calibrated in the field in pH 4 and 7 buffer solutions and checked with a sulfuric acid solution with a theoretical pH of 4 (5×10^{-5} molar H_2SO_4). Rinse probe copiously with sample or deionized water and immerse in sample. Do not stir. The electrode should remain in the sample until there is no discernable drift in the pH reading, but no longer than 15 minutes. At least 10 percent of samples must be measured in replicate. Upon completion of measurement of a sample batch, recheck pH of acid solution.

7.1.2 Laboratory (air-equilibrated) measurement. For normalization of pH values obtained by various participating investigators, air-equilibrated pH measurements should be obtained in the laboratory. Equilibration is achieved by bubbling samples with standard air containing 300 ppm CO_2 for 20 minutes while stirring on a magnetic stirrer. Use an acid-washed (see 3.2.2) fritted glass diffuser for dispersal of air in the sample. Measure pH immediately following equilibration, following procedure in Section 7.1.1. At least 10 percent of samples must be measured in replicate (Ref: Hillman et al.).

7.2 Specific Conductance (μS/cm at 25°C). Measured in the laboratory using a wheatstone bridge type conductivity meter. See Section 8.2 for calibration and QA/QC instructions (Ref: Hillman et al.).

7.3 True color. Comparison of centrifuged sample with platinum-cobalt color standards. (Ref: USEPA, 1979).

7.4 Total alkalinity. Titration with 0.020 N H_2SO_4 using Gran plot calculations. Fixed endpoint titration is not acceptable (Ref: Gran, 1950, 1952; Golterman and Clymo, 1969; Zimmerman and Harvey, 1978-1979; Hillman et al.).

7.5 Calcium, magnesium, sodium, and potassium. Atomic absorption spectrometry, direct aspiration (Ref: USEPA, 1979).

7.6 Sulfate, chloride, nitrate. Ion chromatography (Ref: Hillman et al.).

7.7 Aluminum, total filtered. Graphite furnace atomic absorption (EPA Method 202.2) (Ref: Hillman et al.; USEPA, 1979).

7.8 Phosphorus, total. Colorimetric, automated, block digestor AAII (USEPA, 1979), or USGS colorimetric, phosphomolybdate, automated (Hillman et al.).

7.9 Ammonium. Colorimetric, automated phenate (USEPA, 1979).

7.10 Kjeldahl nitrogen. Colorimetric, automated phenate (USEPA, 1979).

7.11 Table 1 states desired minimum analytical detection limits and within-laboratory relative precision goals.

8.0 QUALITY CONTROL PROCEDURES

Procedures normally followed by participants in the long-term monitoring program should be continued. The intent of this section is to ensure the common use of standardized quality control procedures for comparability of results. Any of the procedures given here that are not now being followed by cooperating agencies or institutions should be added to their QA/QC programs.

8.1 Precision and Accuracy

8.1.1 Precision

8.1.1.1 Definition: Precision is a measure of agreement among individual measurements of the same property, under prescribed similar conditions. In this program we recognize (1) intralaboratory and (2) sampling and analysis precision.

8.1.1.2 Intralaboratory Precision

Intralaboratory precision is determined by analyzing an individual sample in replicate. This should be done for at least one sample per batch for each variable being measured. The difference between the two resultant values is multiplied by 0.89 to approximate the standard deviation. The standard deviation divided by the mean of the duplicate values and multiplied by 100 yields the relative standard deviation (RSD) in percent. The RSD is an operational statistic (also called the coefficient of variation) indicating the dispersion of a set of replicate measurements as a percentage of the mean value. In reporting precision for a given variable, show the number of replicate analyses, range of RSD values, and average RSD.

Table 1. Required minimum analytical detection limits (note reporting units), within-laboratory relative precision, and bias limits. (NOTE: Some listed measurements may not apply to the existing long-term monitoring program. See 2.0).

Parameter (a)	Units	Required Detection Limit	Intralab Relative Precision Goal (%) (b)	Bias Upper Limit (%)
Acidity	µeq/l	5	10	10
Alkalinity	µeq/l	5	10	10
Al, Total	mg/l	0.005	10 Al>0.01), 20 (Al<0.01)	10/20
Ca	µeq/l	0.5	5	10
Cl^-	µeq/l	0.3	5	10
Color	ALPH units	0	± 5 (c)	--
DIC	mg/l	0.05	10	10
DOC	mg/l	0.1	5 (DOC>5), 10 (DOC<5)	10
F^-	µeq/l	0.3	5	10
Fe	mg/l	0.01	10	10
K	µeq/l	0.3	5	10
Mg	µeq/l	0.8	5	10
Mn	mg/l	0.01	10	10
Na	µeq/l	0.4	5	10
NH_4	µeq/l	0.6	5	10
NO_3	µeq/l	0.1	10	10
pH, field	pH units	-	± 0.1 (c)	--
pH, lab	pH units	-	± 0.05 (c)	--
SiO_2	mg/l	0.05	5	10
SO_4^{2-}	µeq/l	1.0	5	10
Specific Conductance	µS/cm	(d)	1	5
Total P	mg/l	0.002	10 (P>0.01), 20 (P<0.01)	10/20

(a) Dissolved ions and metals are determined, except where noted.

(b) Unless otherwise noted, this is the relative precision at concentrations above about 10 times instrumental detection limits.

(c) Absolute precision goal in terms of applicable units.

(d) Blank must be <1.0 µS/cm.

8.1.1.3 Sampling and Analysis Precision

Sampling precision cannot be estimated directly. However, the precision in the combined sampling and analysis procedure can be estimated from the analysis of the duplicate samples taken in the field (see 6.1). Then the sampling variance can be estimated by subtracting the analytical variance obtained in 8.1.1.2. The precision in the combined sampling and analysis operation is estimated by applying the same methodology described for intralaboratory precision (8.1.1.2).

8.1.2 Accuracy

8.1.2.1 Definition: Accuracy is a measure of the closeness of an individual measurement or an average of a number of measurements to the true values. Accuracy includes both precision and recovery and can be expressed as a percent recovery or percent bias interval.

8.1.2.2 Evaluation of Accuracy

Two approaches are specified:

8.1.2.2.1 Fortify an actual sample with a known amount of material, analyze the fortified (spiked) sample, and calculate the percent recovery. This should be done for at least one sample per batch for each variable being measured. In reporting accuracy for a given variable, show the number of spiked analyses, concentration of spike, range of bias (+ and - percent), and average bias (+ or - percent).

8.1.2.2.2 Audit samples are provided three times each year by an independent contractor. Analysis results are compared with the known concentrations to determine (1) intralaboratory bias and (2) comparability of measurements among the various monitoring projects.

8.2 Cautions Regarding Specific Conductance and Alkalinity

8.2.1 Specific Conductance

After calibration and prior to measuring the first sample, measure the conductance of a QC standard. The standard should have a theoretical or certified conductance of about 50 μS/cm (0.0005000 M KCl has a conductance of 73.90 μS/cm at 25°C). It must be prepared from a stock solution that is different from that from which the calibration standard is prepared. If the measured conductivity is not within ± 1 percent of the certified value, then restandardize the meter and cell and repeat the measurement.

Remeasure the conductance of the QC standard at least once every 10 samples. One sample per batch must be measured in duplicate.

8.2.2 Alkalinity

At least 10 percent of alkalinity titrations must be run in replicate. Agreement must be ± 10 percent or less. If not, run a third determination.

8.3 Further Procedural Checks

Once each variable in a sample has been determined, there are several procedures which must be followed to check the correctness of the analyses. These are outlined below.

8.3.1 Cation-Anion Balance

Theoretically, the sum of equivalents of anions equals the sum of equivalents of cations in a sample. In practice, this rarely occurs due to analytical variability and ions which are present but not measured. For each sample, the sums of the measured anion and cation equivalents, total ion strength, and ion percent difference are calculated as follows:

$$\sum \text{anions} = [Cl^-] + [F^-] + [NO_3^-] + [SO_4^{2-}] + [HCO_3^-] + [CO_3^{2-}]$$

$$\sum \text{cations} = [Na^+] + [K^+] + [Ca^{2+}] + [Mg^{2+}] + [NH_4^+] + [H^+]$$

$$\%\ \text{Ion Difference} = \frac{\sum \text{anions} - \sum \text{cations}}{\sum \text{anions} + \sum \text{cations}} \times 100$$

$$\text{Total ion strength} = \sum \text{anions} + \sum \text{cations}$$

[Omission of F^-, CO_3^{2-}, and NH_4^+ will not significantly affect results. Alkalinity plus H^+ (calculated from pH) may be used for HCO_3^-].

All concentrations are expressed as microequivalents/liter (μeq/l). Table 2 lists factors for converting mg/l to μeq/l for each of the parameters.

Samples which have a poor ion balance may have to be reanalyzed. Table 3 lists the reanalysis criteria.

8.3.2 Specific Conductance Balance

An estimate of the specific conductance of a sample can be calculated by summing the equivalent conductance values for each measured ion at infinite dilution.

The calculated conductance is determined by multiplying the concentration of each ion (in μeq/l) by the appropriate factor (F) in Table 4.

The calculated conductance for the entire sample is obtained from the relationship,

$$\text{Calculated Conductance} = \frac{\sum (\text{F x Conc. in } \mu\text{eq/l})}{1000}$$

The percent difference between measured conductance and calculated conductance is given by

$$\text{\% Conductance Difference} = \frac{\text{Calculated - Measured}}{\text{Measured}} \text{ x } 100$$

Samples which have percent conductance differences exceeding the limits listed in Table 3 may have to be reanalyzed.

Table 2. Factors to convert mg/l to μeq/l

Ion	Factor (μeq/l per mg/l)
Ca^{2+}	49.9
Cl^-	28.2
$CO_3{}^{2-}$	33.3
F^-	52.6
K^+	25.6
Mg^{2+}	82.3
Na^+	43.5
$NH_4{}^+$	55.4
$NO_3{}^-$	16.1
$SO_4{}^{2-}$	20.8
Alkalinity (as $CaCO_3$)	20.0

Table 3. Chemical reanalysis criteria

A. Cation-Anion Balance

Total Ion Strength (μeq/l)	% Ion Difference*
< 50	> ± 60
≥ 50 < 100	> ± 30
≥ 100	> ± 15

B. Calculated vs. Measured Conductance

Measured Conductance (μS/cm)	% Conductance Difference*
< 5	> 50
≥ 5 < 30	> 30
≥ 30	> 20

* If the percent difference exceeds these values, the sample is reanalyzed. When reanalysis is indicated, the data for each parameter are examined for possible analytical error. Any suspect parameters are then reanalyzed and the above percent differences recalculated.

Table 4. Conductance factors (F) of ions

Ion[a]	Conductance (μS/cm at 25°C) per μeq/l	Ion[a]	Conductance (μS/cm at 25°C) per μeq/l
Ca^{2+}	0.052	NO_3^-	0.071
Mg^{2+}	0.047	Cl^-	0.076
Na^+	0.049	SO_4^{2-}	0.074
K^+	0.072	HCO_3^-	0.044
H^+	0.350	OH^-	0.198
NH_4^+	0.075		

[a] H^+ and OH^- calculated as: $[H^+] = 10\text{-pH} \times 10^6$ μeq/l.

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APPENDIX B

LAKES PRESENTLY INCLUDED IN THE LONG-TERM MONITORING PROGRAM

Name	State	Latitude	Longitude	Elev. (m)	Lake[1] Type	Lake Area (ha)
			Adirondacks			
Arbutus Lake	NY	43°58′00″N	74°14′00″W	513	Drainage	50.2
Barnes Lake	NY	43°34′00″N	75°13′40″W	393	Seepage	2.5
Big Moose Lake	NY	43°49′45″N	74°51′00″W	556	Drainage	503.5
Black Lake	NY	44°26′00″N	74°18′00″W	494	Drainage	31.5
Bubb Lake	NY	43°46′15″N	74°51′15″W	553	Drainage	18.5
Cascade Lake	NY	43°47′28″N	74°48′15″W	553	Drainage	36.9
Clear Pond	NY	44°00′00″N	73°49′20″W	582	Closed	70.6
Constable Lake	NY	43°49′00″N	74°50′00″W	582	Drainage	22.7
Dart Lake	NY	43°47′50″N	74°51′30″W	536	Drainage	49.8
Heart Lake	NY	44°10′56″N	73°58′10″W	660	Drainage	11.1
Lake Rondaxe	NY	43°45′50″N	74°54′20″W	524	Closed	68.2
Little Echo Pond	NY	44°18′20″N	74°21′27″W	482	Seepage	0.9
Moss Lake	NY	43°47′10″N	74°51′00″W	536	Closed	44.9
Otter Lake	NY	43°11′17″N	74°30′00″W	503	Drainage	16.2
Squash Pond	NY	43°49′35″N	74°53′23″W	649	Drainage	1.7
West Pond	NY	43°48′40″N	74°52′45″W	579	Drainage	8.9
Windfall Lake	NY	43°49′00″N	74°51′00″W	595	Drainage	1.5
			Vermont			
Beaver Pond	VT	45°00′20″N	71°56′30″W	468	Drainage	18.2
Beebe Pond	VT	43°03′12″N	73°01′58″W	719	Drainage	3.5
Big Mud Pond	VT	43°18′50″N	72°55′50″W	789	Drainage	6.0
Big Muddy Pond	VT	44°45′20″N	72°36′00″W	430	Drainage	5.4
Bourn Pond	VT	43°06′20″N	73°00′10″W	778	Drainage	19.9
Branch Pond	VT	43°04′52″N	73°01′07″W	802	Closed	17.2
Cole Pond	VT	43°08′55″N	72°48′20″W	364	Seepage	15.2
Cow Mountain Pond	VT	44°33′40″N	71°42′10″W	629	Drainage	3.1
Forester Pond	VT	43°04′54″N	72°52′05″W	533	Seepage	3.2
Griffith Lake	VT	43°18′08″N	72°57′35″W	789	Drainage	6.0
Grout Pond	VT	43°02′44″N	72°56′45″W	681	Seepage	32.9
Hardwood Pond	VT	44°28′05″N	72°30′00″W	478	Drainage	19.0
Haystack Pond	VT	42°55′00″N	72°55′00″W	910	Drainage	10.8
Holland Pond	VT	44°59′10″N	71°55′45″W	436	Drainage	131.4

[1] Lake Types: Drainage = with an outlet, may or may not have an inlet.
Closed = with an inlet, no outlet.
Seepage = no inlet or outlet.
Reservoir = a drainage lake with a flow control structure.

LAKES PRESENTLY INCLUDED IN THE LONG-TERM MONITORING PROGRAM

Name	State	Latitude	Longitude	Elev. (m)	Lake[1] Type	Lake Area (ha)
Vermont						
Howe Pond	VT	42°47′08"N	72°19′15"W	587	Drainage	20.9
Kettle Pond	VT	44°17′40"N	72°19′08"W	440	Drainage	43.7
Lake Mansfield	VT	44°28′20"N	72°49′00"W	351	Reservoir	15.6
Lake Ninevah	VT	43°28′15"N	72°45′30"W	535	Drainage	69.2
Levi Pond	VT	44°16′00"N	72°13′40"W	497	Drainage	9.2
Lily Pond	VT	43°14′03"N	72°45′05"W	454	Drainage	11.4
Little Averill Pond	VT	44°57′18"N	71°43′00"W	530	Drainage	183.2
Little Pond (Woodford)	VT	42°55′30"N	73°03′55"W	793	Drainage	7.1
Little Pond (Winhall)	VT	43°07′25"N	72°56′30"W	753	Seepage	5.4
Little Rock Pond	VT	43°24′00"N	72°57′20"W	565	Drainage	6.1
Moses Pond	VT	43°20′03"N	72°50′35"W	680	Drainage	2.6
Osmore Pond	VT	44°18′30"N	72°16′45"W	448	Drainage	18.7
Pigeon Pond	VT	44°14′45"N	72°19′45"W	596	Drainage	29.0
Somerset Reservoir	VT	43°00′00"N	72°56′20"W	650	Reservoir	597.7
South Pond	VT	42°50′38"N	72°42′45"W	506	Drainage	25.2
Stamford Pond	VT	42°49′20"N	73°03′55"W	753	Drainage	3.6
Sterling Pond	VT	44°33′22"N	72°46′28"W	917	Drainage	2.7
Stratton Pond	VT	43°06′15"N	72°58′10"W	779	Seepage	17.7
Sucker Pond	VT	42°49′30"N	73°07′45"W	691	Drainage	21.2
Sunset Lake	VT	42°55′10"N	72°41′00"W	421	Drainage	37.7
Unknown Pond	VT	44°54′35"N	71°50′40"W	710	Drainage	6.7
Wheeler Pond	VT	44°42′30"N	71°38′30"W	313	Drainage	28.3
Maine						
Anderson Pond	ME	44°38′52"N	68°03′35"W	70	Drainage	4.8
Little Long Pond	ME	44°38′15"N	68°04′41"W	70	Drainage	24.7
Mud Pond	ME	44°37′59"N	68°05′27"W	101	Drainage	1.6
Salmon Pond	ME	44°37′53"N	68°05′10"W	88	Drainage	2.6
Spring River Lake	ME	44°37′10"N	68°03′00"W	57	Drainage	270.6
Tilden Pond	ME	44°38′05"N	68°04′20"W	70	Drainage	15.4
Upper Midwest						
Andrus Lake	MI	46°42′00"N	85°02′22"W	624	Seepage	12.6

[1] Lake Types: Drainage = with an outlet, may or may not have an inlet.
Closed = with an inlet, no outlet.
Seepage = no inlet or outlet.
Reservoir = a drainage lake with a flow control structure.

LAKES PRESENTLY INCLUDED IN THE LONG-TERM MONITORING PROGRAM

Name	State	Latitude	Longitude	Elev. (m)	Lake[1] Type	Lake Area (ha)
			Upper Midwest			
Bass Lake	MI	46°27′50"N	85°43′00"W	273	Drainage	58.3
Buckeye Lake	MI	46°27′57"N	85°44′19"W	274	Closed	47.7
Chris Brown Lake	MI	46°37′34"N	85°30′27"W	215	Drainage	23.7
Cusino Lake	MI	46°27′16"N	86°15′30"W	267	Seepage	54.9
Johnson Lake	MI	46°25′30"N	85°02′38"W	252	Seepage	16.7
Kelly Lake	MI	46°26′24"N	85°38′45"W	255	Seepage	12.3
McNearney Lake	MI	46°25′35"N	84°57′30"W	264	Seepage	49.8
Monocle Lake	MI	46°28′30"N	84°38′45"W	195	Closed	69.1
Murray Lake	MI	46°28′15"N	85°42′05"W	272	Drainage	37.9
Nevins Lake	MI	46°31′00"N	86°14′35"W	278	Seepage	109.1
Stuart Lake	MI	46°35′24"N	85°30′35"W	245	Seepage	29.7
Chester Lake	MN	47°59′03"N	90°05′00"W	572	Drainage	19.7
Cruiser Lake	MN	48°29′54"N	92°48′19"W	380	Seepage	47.8
Crum Lake	MN	47°51′50"N	93°18′37"W	415	Seepage	6.3
Franklin Lake	MN	48°18′00"N	92°37′00"W	366	Drainage	60.7
Locator Lake	MN	48°32′26"N	93°00′13"W	348	Drainage	54.4
Loiten Lake	MN	48°31′33"N	92°55′24"W	362	Drainage	39.1
Long Lake	MN	48°18′25"N	92°43′30"W	372	Drainage	193.0
Moon lake	MN	47°32′20"N	93°29′40"W	430	Seepage	10.3
Shoepack Lake	MN	48°30′13"N	92°53′00"W	364	Drainage	123.3
Spring Lake	MN	48°22′22"N	92°37′48"W	354	Drainage	89.8
Camp Twelve Lake	WI	45°59′03"N	89°22′14"W	501	Closed	21.6
Clear Lake	WI	45°22′00"N	89°13′50"W	519	Seepage	35.2
Greater Bass Lake	WI	45°21′25"N	89°11′30"W	512	Closed	100.0
Lake Clara	WI	45°30′44"N	89°34′15"W	462	Seepage	34.0
Little Rock Lake	WI	45°59′55"N	89°42′15"W	495	Seepage	15.7
Long Lake	WI	45°43′00"N	89°36′15"W	483	Seepage	45.7
Luna Lake	WI	45°54′19"N	88°57′35"W	518	Seepage	25.6
McGrath Lake	WI	45°47′30"N	89°38′40"W	484	Seepage	20.7
Morgan Lake	WI	45°46′27"N	88°32′35"W	447	Seepage	17.4
Nichols Lake	WI	46°06′14"N	89°41′15"W	495	Seepage	15.0
Sand Lake	WI	45°43′28"N	89°39′05"W	484	Seepage	15.1
Sugar Camp Lake	WI	45°48′00"N	89°18′15"W	506	Seepage	210.2
Sunset Lake	WI	45°55′35"N	89°20′15"W	497	Seepage	83.2
Vandercook Lake	WI	45°58′55"N	89°41′13"W	497	Seepage	39.4

[1] Lake Types: Drainage = with an outlet, may or may not have an inlet.
Closed = with an inlet, no outlet.
Seepage = no inlet or outlet.
Reservoir = a drainage lake with a flow control structure.

LAKES PRESENTLY INCLUDED IN THE LONG-TERM MONITORING PROGRAM

Name	State	Latitude	Longitude	Elev. (m)	Lake[1] Type	Lake Area (ha)
Southern Blue Ridge Province						
Blue Ridge Lake	GA	34°51′45"N	84°16′00"W	515	Reservoir	1279.6
Winfield Scott Lake	GA	34°44′21"N	83°58′25"W	875	Reservoir	5.4
Chatuge Lake	NC	35°00′45"N	83°47′15"W	587	Reservoir	2861.9
Lake Logan	NC	35°25′00"N	82°55′40"W	887	Reservoir	35.2
Mars Hill Lake	NC	35°56′40"N	82°29′40"W	1164	Reservoir	2.0
Price Lake	NC	36°08′15"N	81°44′00"W	1030	Reservoir	14.7
Ravenel (Cullasaja) L.	NC	35°05′07"N	83°09′40"W	1213	Reservoir	8.2
Santeetlah Lake	NC	35°22′00"N	83°52′30"W	591	Reservoir	1034.5
Thunder Lake	NC	35°07′50"N	82°39′55"W	896	Reservoir	19.9
Wolf Creek Reservoir	NC	35°16′05"N	82°58′10"W	1082	Reservoir	2.0
Miller Lake	TN	36°10′42"N	82°09′23"W	1103	Reservoir	3.0
Watauga Lake	TN	36°19′40"N	82°05′00"W	597	Reservoir	2535.1
Colorado Rockies						
Big Eldorado	CO	37°42′48"N	107°32′36"W	3812	Drainage	5.7
Lake Elbert	CO	40°38′03"N	106°42′25"W	3290	Drainage	4.4
Little Eldorado	CO	37°42′48"N	107°32′45"W	3813	Drainage	1.0
Long Lake	CO	40°28′33"N	106°41′24"W	3000	Drainage	15.8
Lower Sunlight	CO	37°38′04"N	107°34′43"W	3669	Drainage	6.2
Seven Lakes	CO	40°53′44"N	106°40′51"W	3272	Drainage	18.1
Summit Lake	CO	40°32′45"N	106°40′49"W	3145	Drainage	2.3
Upper Grizzly	CO	37°37′19"N	107°23′05"W	3990	Drainage	3.1
Upper Sunlight	CO	37°37′40"N	107°34′47"W	3825	Drainage	5.2
White Dome	CO	37°42′32"N	107°33′09"W	3826	Drainage	1.8

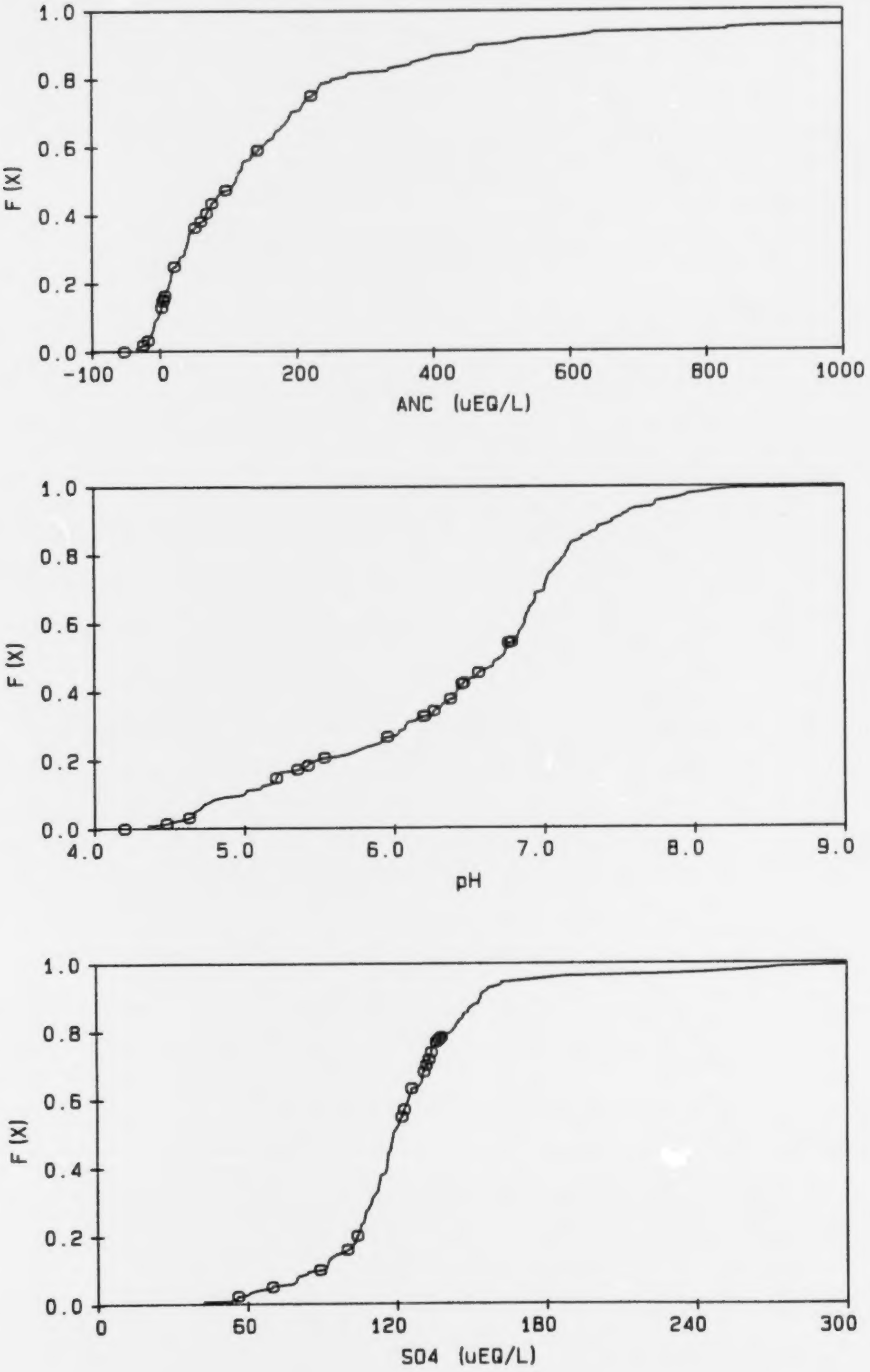
[1] Lake Types:
Drainage = with an outlet, may or may not have an inlet.
Closed = with an inlet, no outlet.
Seepage = no inlet or outlet.
Reservoir = a drainage lake with a flow control structure.

APPENDIX C

CUMULATIVE DISTRIBUTION FREQUENCY CURVES (F(x) CURVES)

This appendix contains a complete set of cumulative distribution frequency curves (F(x) curves). Data from the National Lake Survey (NLS) were used to produce the F(x) curves for each subregion. Open circles represent Long-Term Monitoring (LTM) lake data from the same season as the NLS data. See Sections 2.3.2.1 and 3.2.1 for more information. The diagrams are grouped according to subregion.

1A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0.6
0.4
0.2
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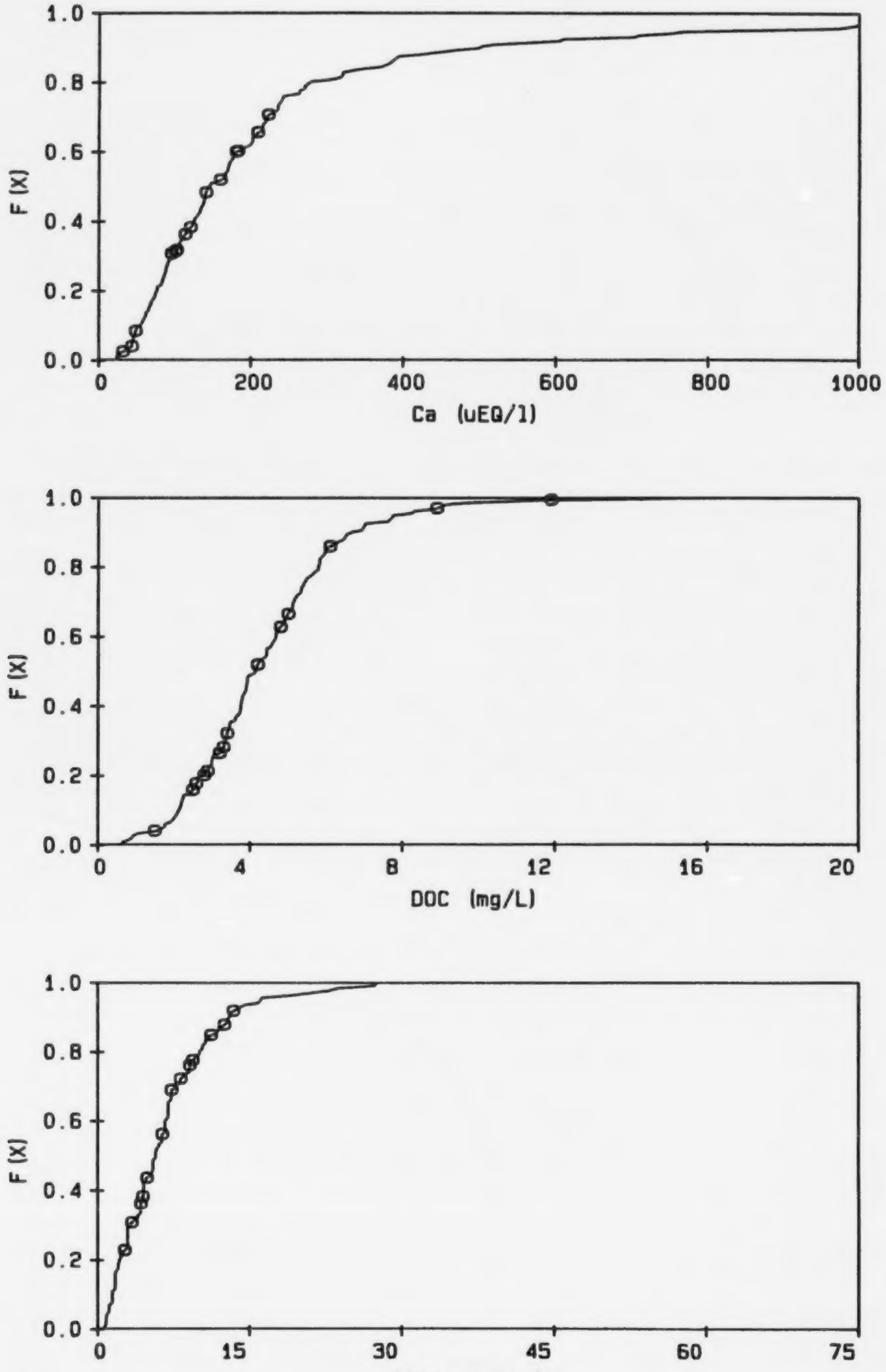
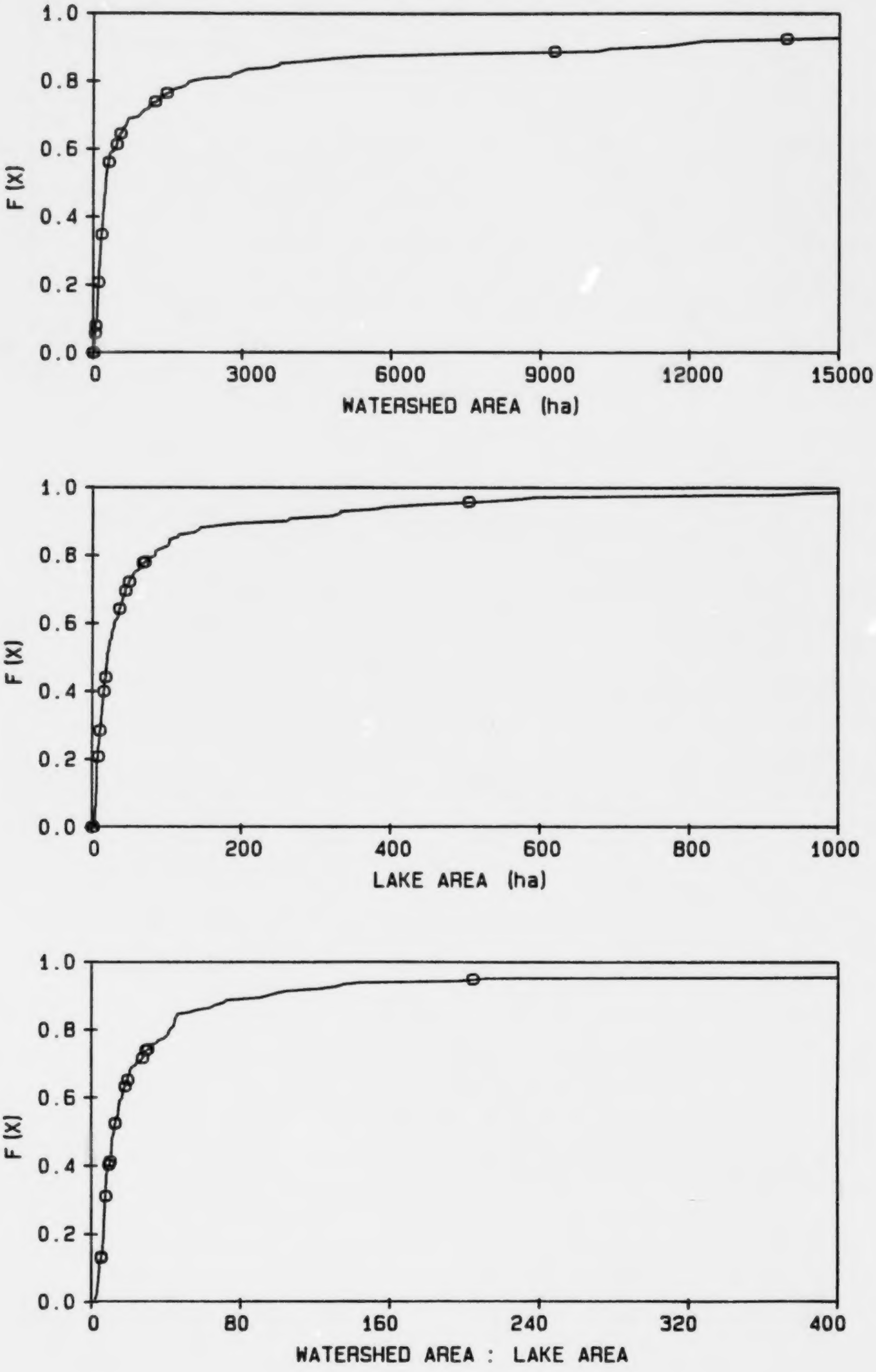
200
400
600
800
1000
ANC (uEQ/L)
F (X)
1.0
0.8
0.6
0.4
0.2
0.0
4.0
5.0
6.0
7.0
8.0
9.0
pH
F (X)
1.0
0.8
0.6
0.4
0.2
0.0
0
60
120
180
240
300
SO4 (uEQ/L)

1A



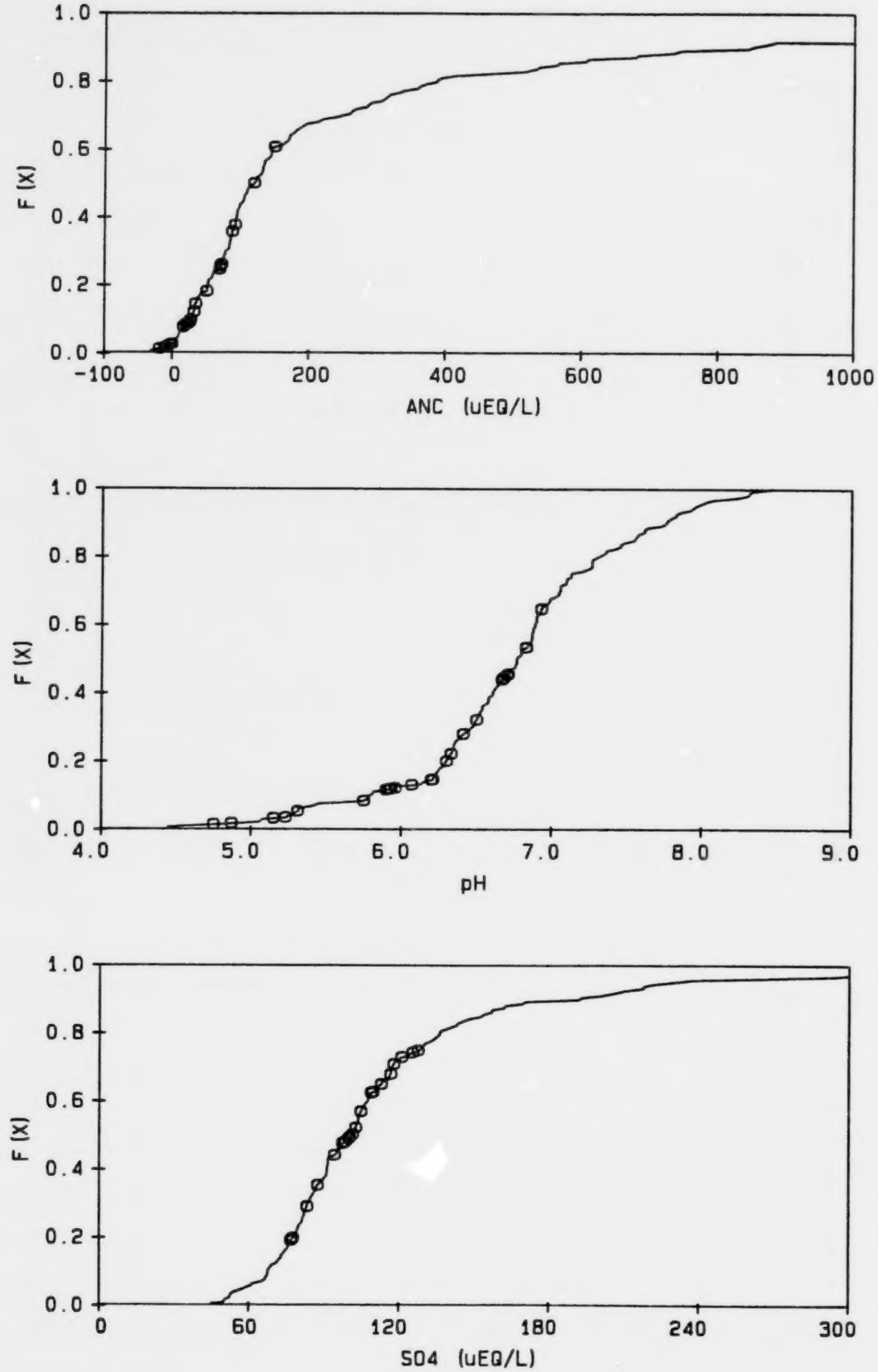
1.0
0.8
0.6
0.4
0.2
0.0
F (X)
0
200
400
600
800
1000
Ca (uEQ/l)
1.0
0.8
0.6
0.4
0.2
0.0
F (X)
0
4
8
12
16
20
DOC (mg/L)
1.0
0.8
0.6
0.4
0.2
0.0
F (X)
0
15
30
45
60
75
SITE DEPTH (m)

1A



F (X)
1.0
0.8
0.6
0.4
0.2
0.0
0
3000
6000
9000
12000
15000
WATERSHED AREA (ha)
F (X)
1.0
0.8
0.6
0.4
0.2
0.0
0
200
400
600
800
1000
LAKE AREA (ha)
F (X)
1.0
0.8
0.6
0.4
0.2
0.0
0
80
160
240
320
400
WATERSHED AREA : LAKE AREA

1C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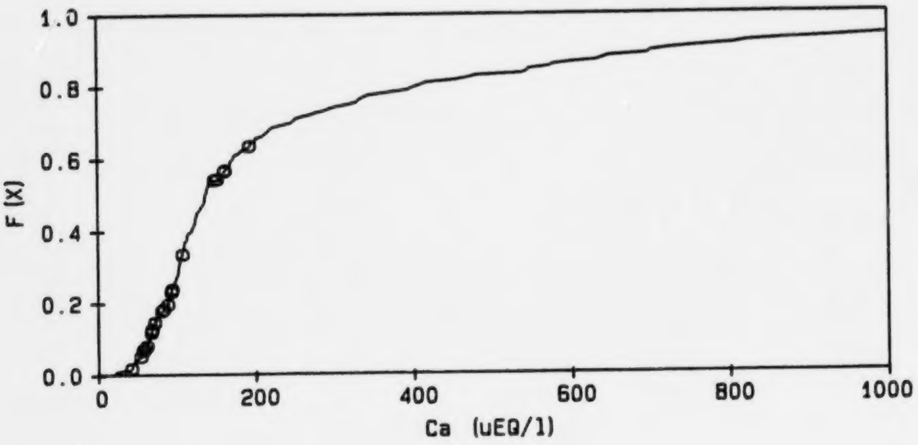
-100
0
200
400
600
800
1000
ANC (uEQ/L)
F (X)
1.0
0.8
0.6
0.4
0.2
0.0
4.0
5.0
6.0
7.0
8.0
9.0
pH
F (X)
1.0
0.8
0.6
0.4
0.2
0.0
0
60
120
180
240
300
SO4 (uEQ/L)

1C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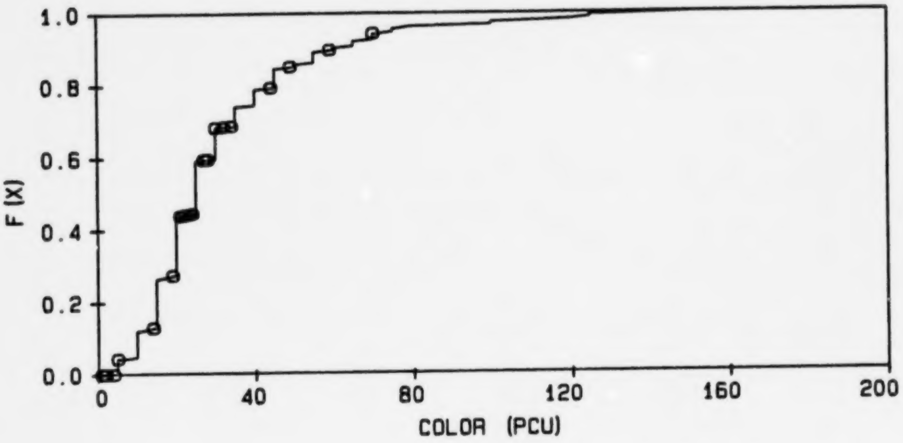
200
400
600
800
1000
Ca (uEQ/l)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0.2
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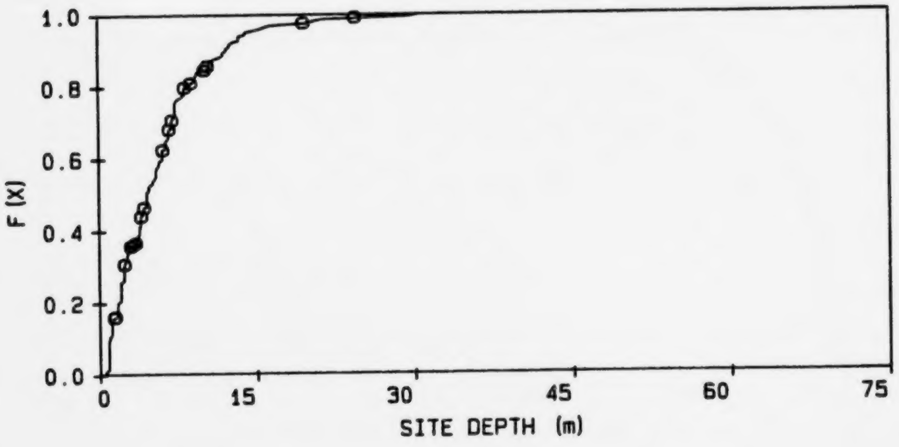
0
40
80
120
160
200
COLOR (PCU)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0.4
0.2
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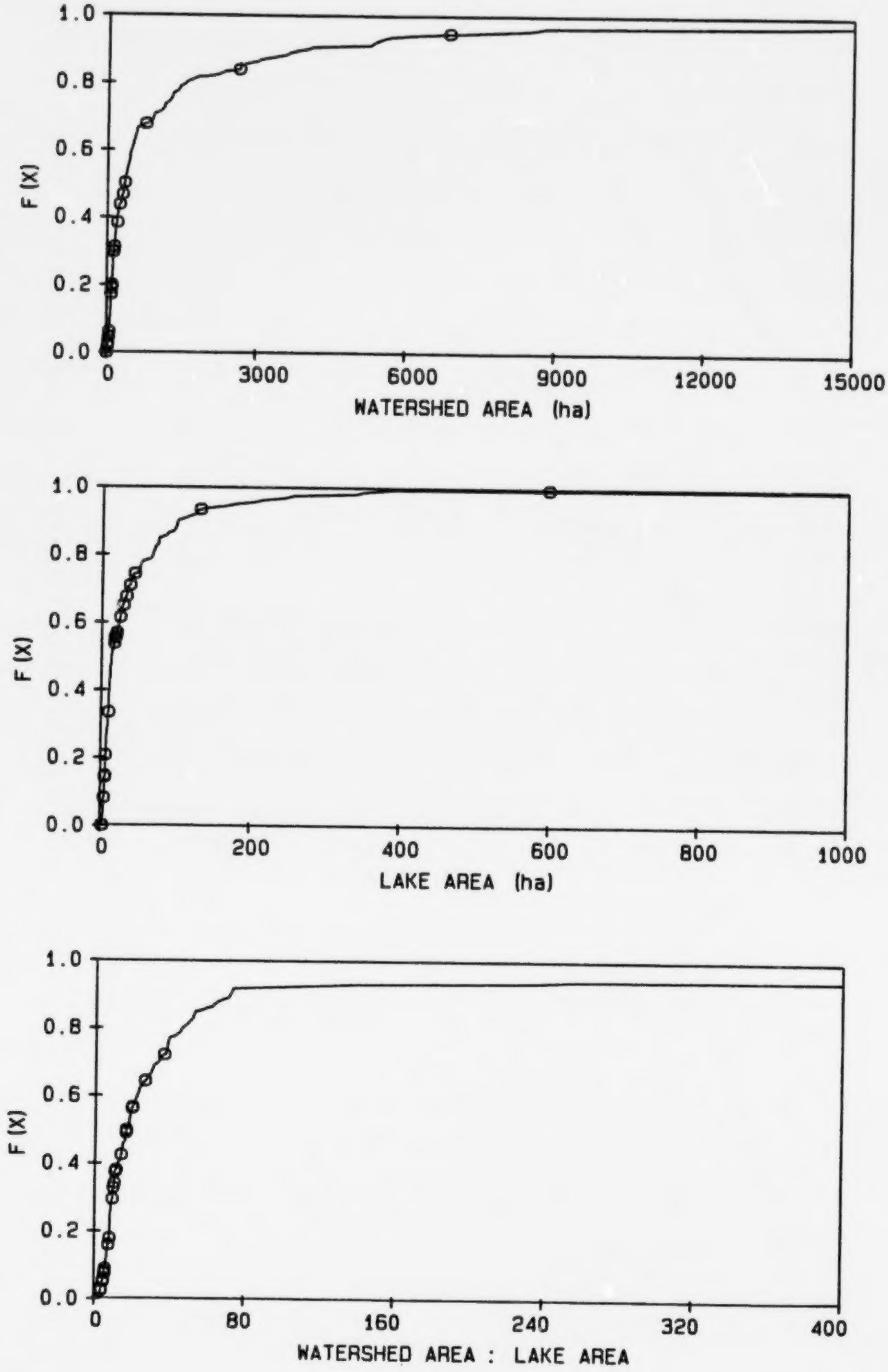
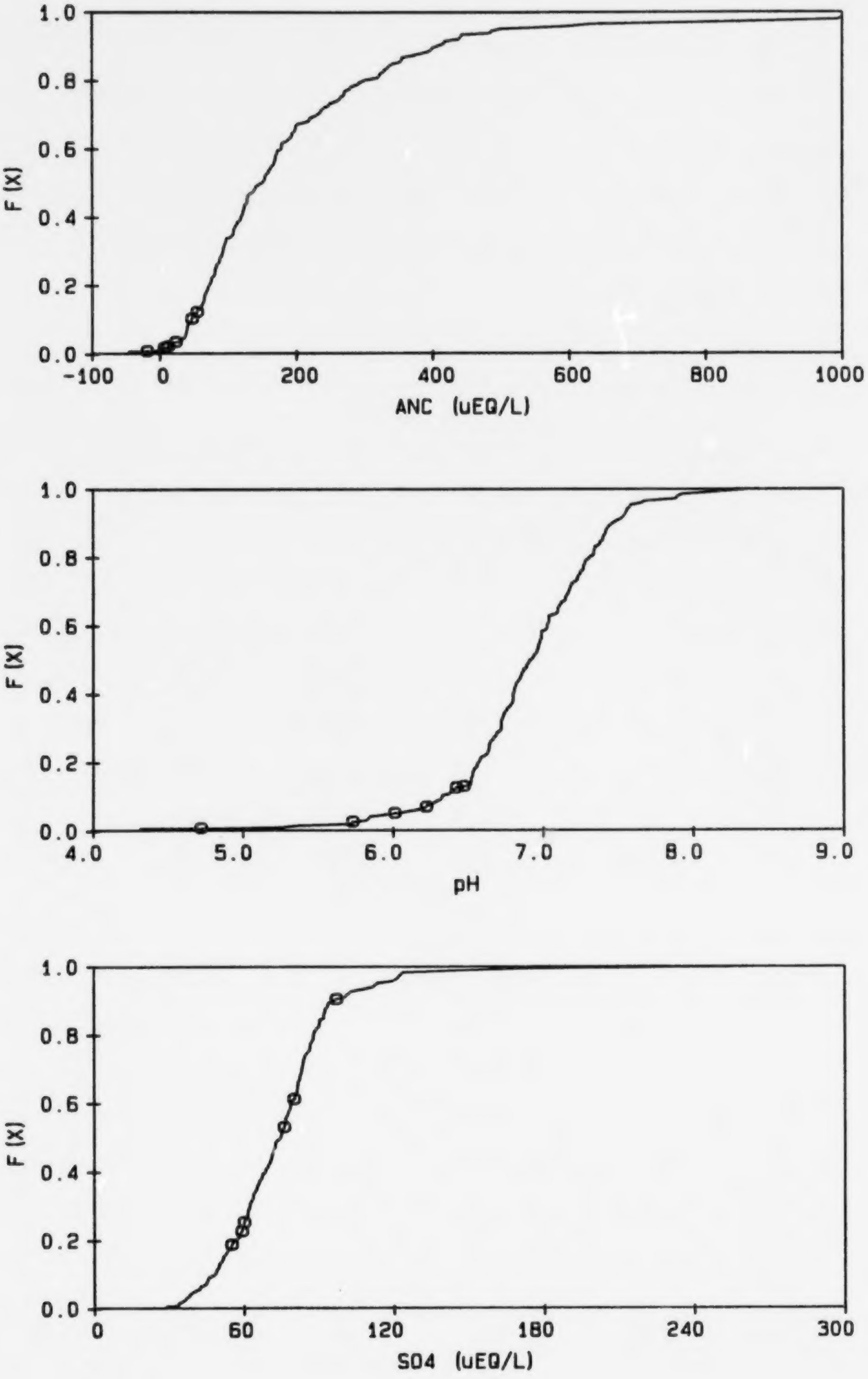
0
15
30
45
60
75
SITE DEPTH (m)

1C


1.0
0.8
0.6
0.4
0.2
0.0
F (X)
0
3000
6000
9000
12000
15000
WATERSHED AREA (ha)
1.0
0.8
0.6
0.4
0.2
0.0
F (X)
0
200
400
600
800
1000
LAKE AREA (ha)
1.0
0.8
0.6
0.4
0.2
0.0
F (X)
0
80
160
240
320
400
WATERSHED AREA : LAKE AREA

1E


F (X)
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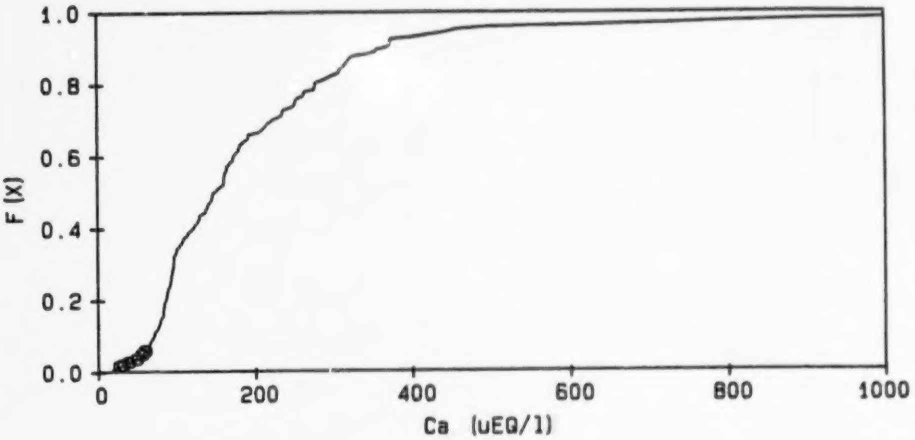
0.8
0.6
0.4
0.2
0.0
-100
0
200
400
600
800
1000
ANC (uEQ/L)
F (X)
1.0
0.8
0.6
0.4
0.2
0.0
4.0
5.0
6.0
7.0
8.0
9.0
pH
F (X)
1.0
0.8
0.6
0.4
0.2
0.0
0
60
120
180
240
300
SO4 (uEQ/L)

1E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0.4
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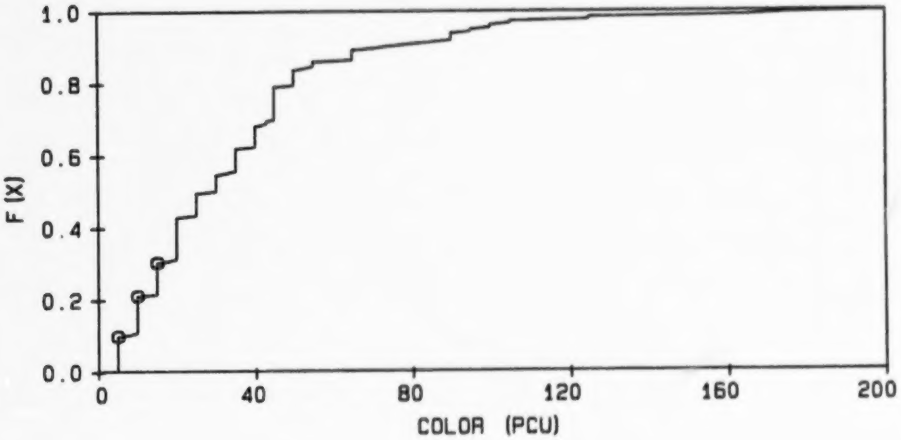
0.0
F (X)
0
200
400
600
800
1000
Ca (uEQ/l)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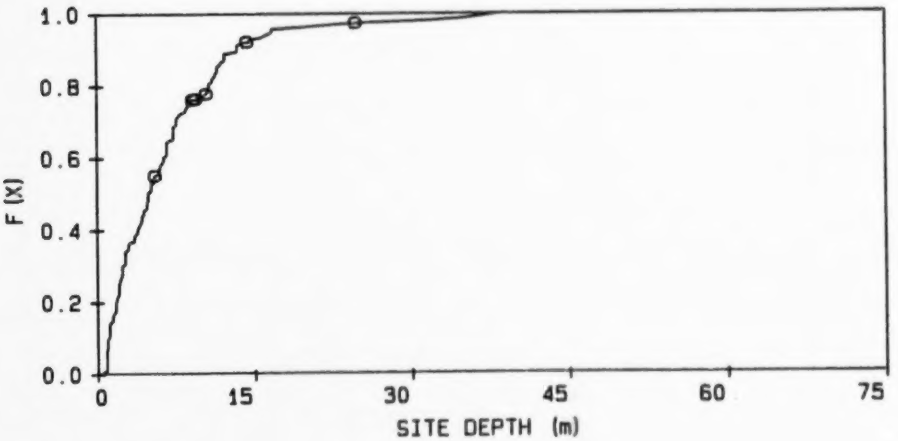
0.8
0.6
0.4
0.2
0.0
F (X)
0
40
80
120
160
200
COLOR (PCU)


1.0
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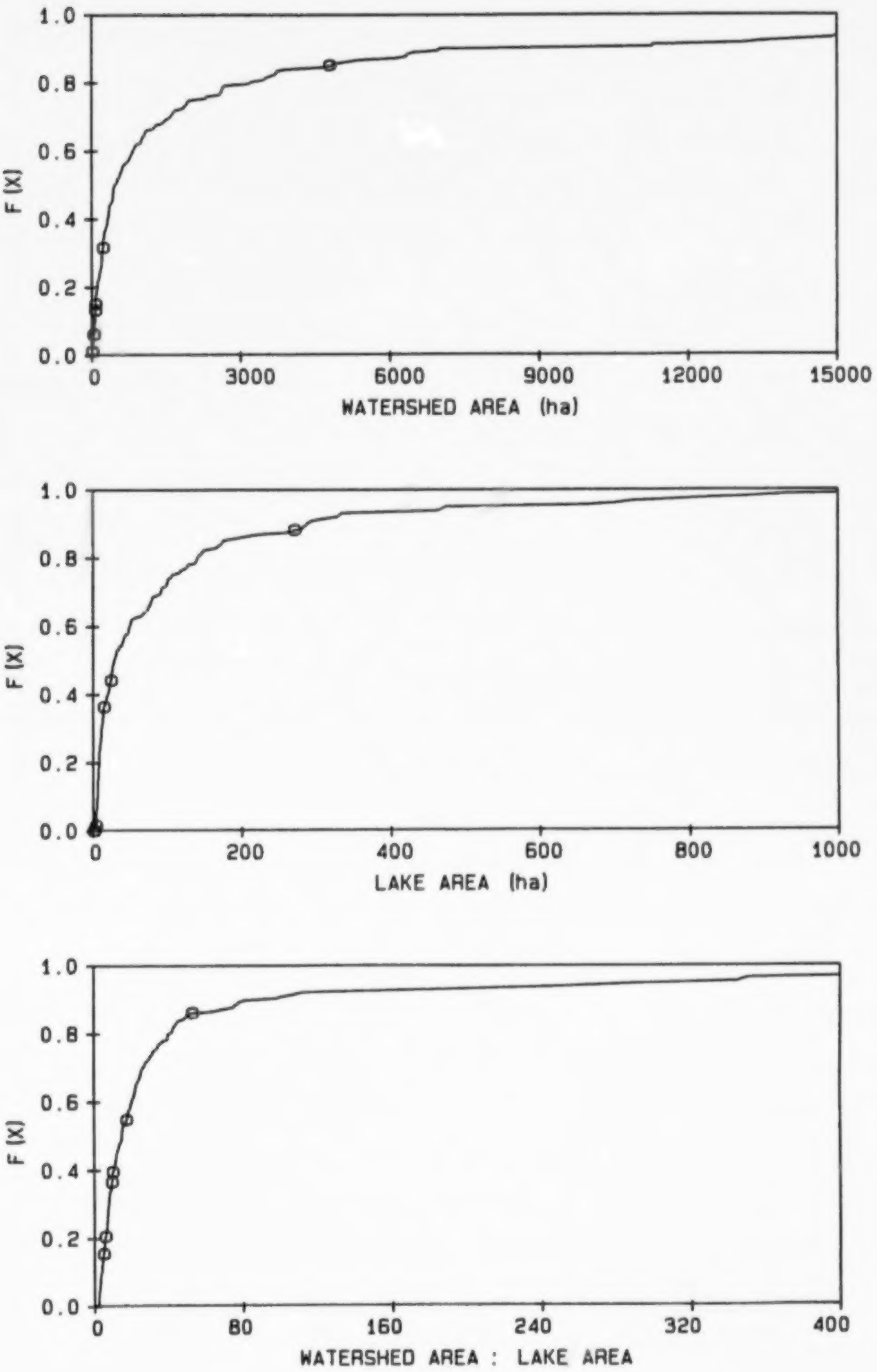
F (X)
0
15
30
45
60
75
SITE DEPTH (m)

1E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0.8
0.6
0.4
0.2
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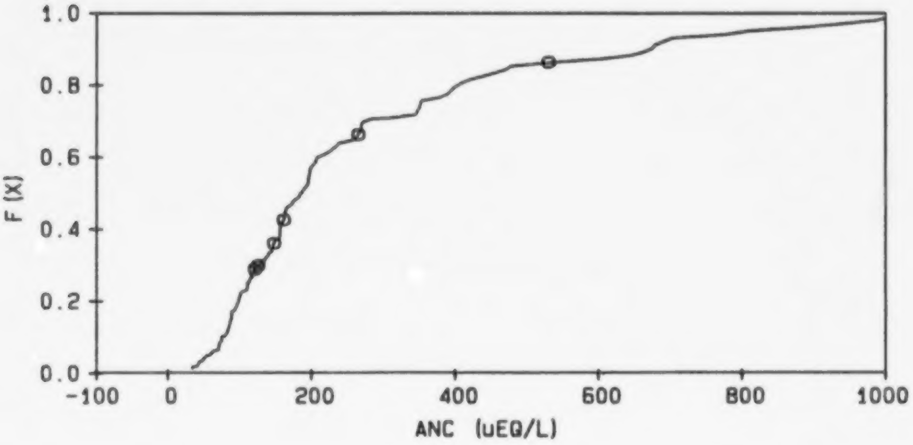
0
3000
6000
9000
12000
15000
WATERSHED AREA (ha)
F (X)
1.0
0.8
0.6
0.4
0.2
0.0
0
200
400
600
800
1000
LAKE AREA (ha)
F (X)
1.0
0.8
0.6
0.4
0.2
0.0
0
80
160
240
320
400
WATERSHED AREA : LAKE AREA

2A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0.0
F (X)
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0
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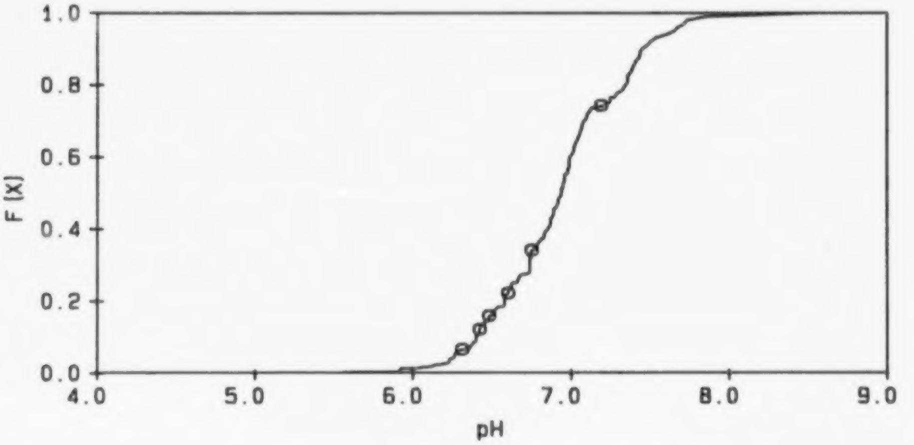
400
600
800
1000
ANC (uEQ/L)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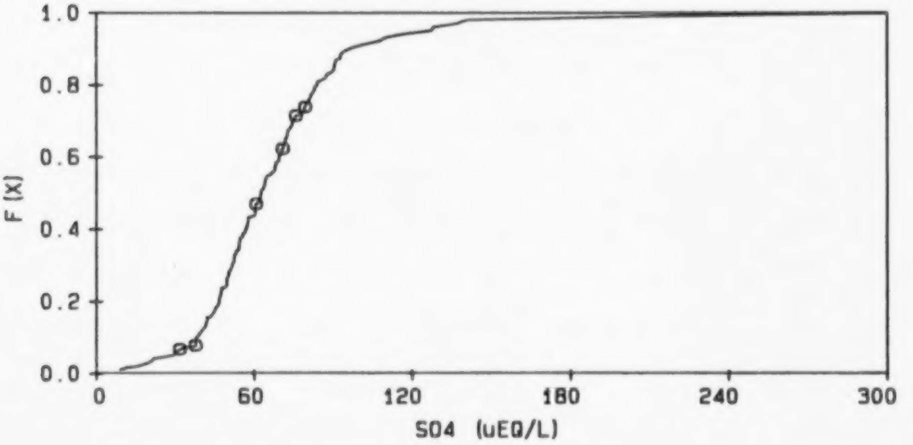
4.0
5.0
6.0
7.0
8.0
9.0
pH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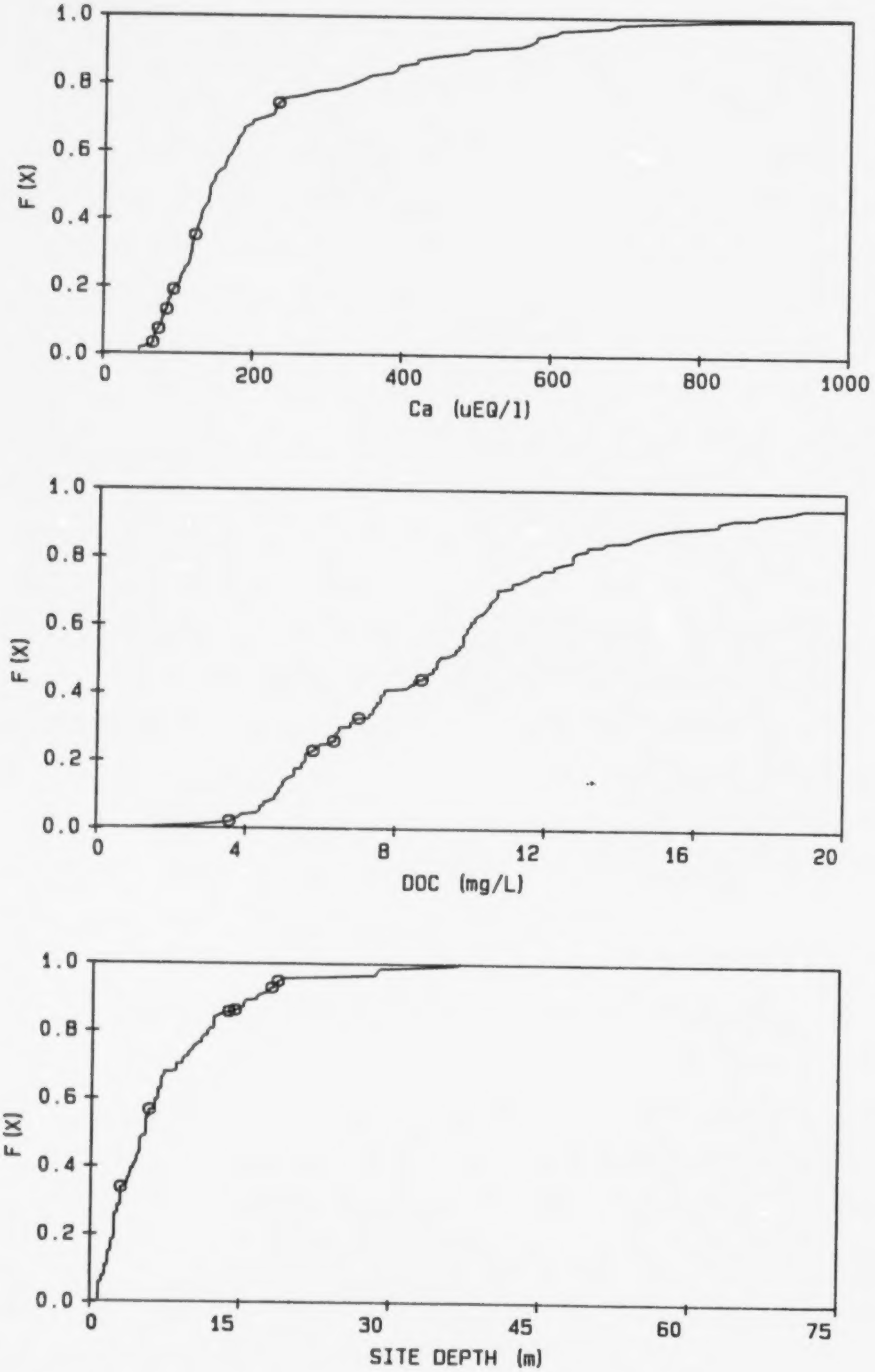
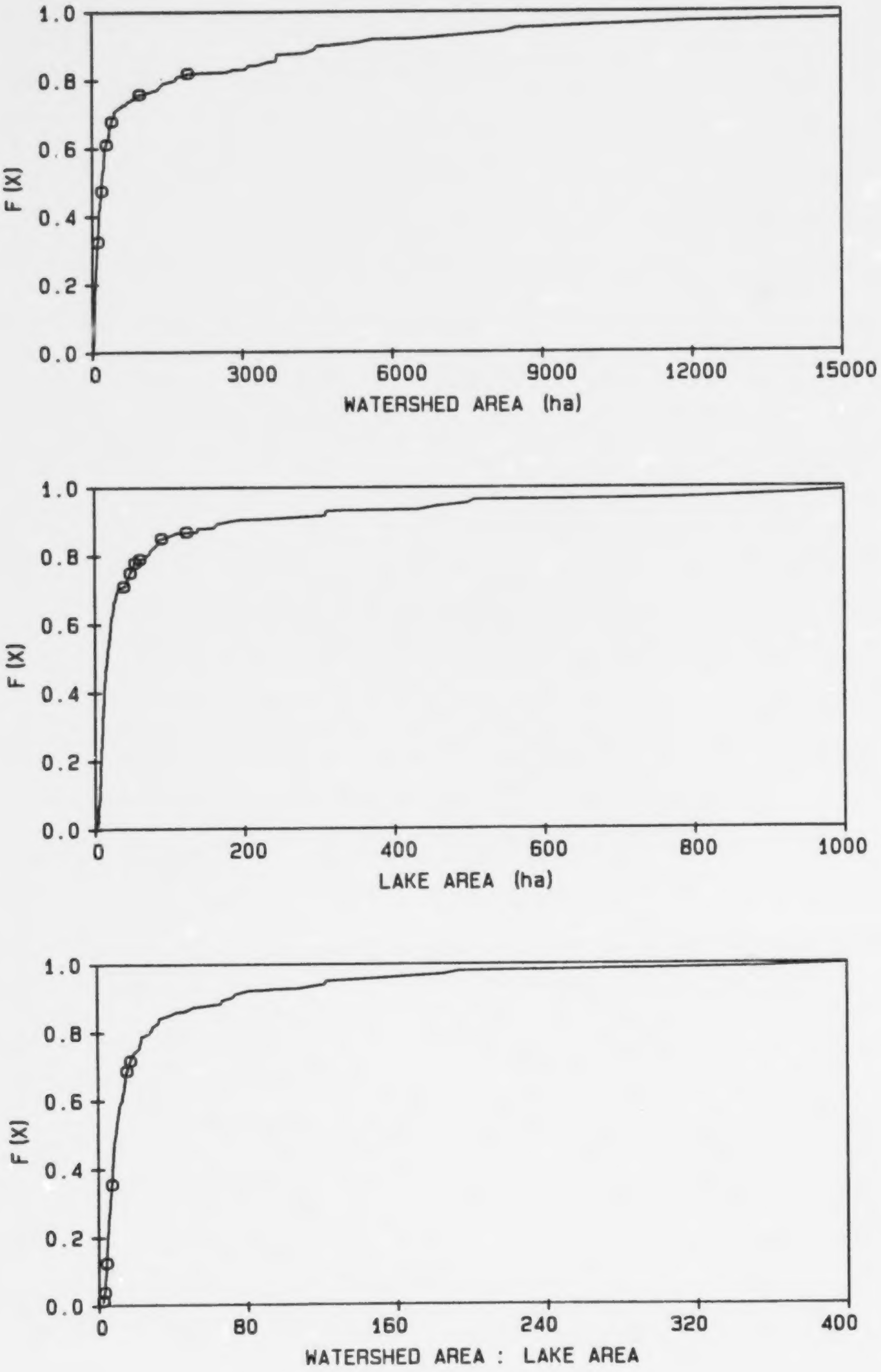
0.0
F (X)
0
60
120
180
240
300
SO4 (uEQ/L)

2A



F (X)
1.0
0.8
0.6
0.4
0.2
0.0
0
200
400
600
800
1000
Ca (uEQ/l)
F (X)
1.0
0.8
0.6
0.4
0.2
0.0
0
4
8
12
16
20
DOC (mg/L)
F (X)
1.0
0.8
0.6
0.4
0.2
0.0
0
15
30
45
60
75
SITE DEPTH (m)

2A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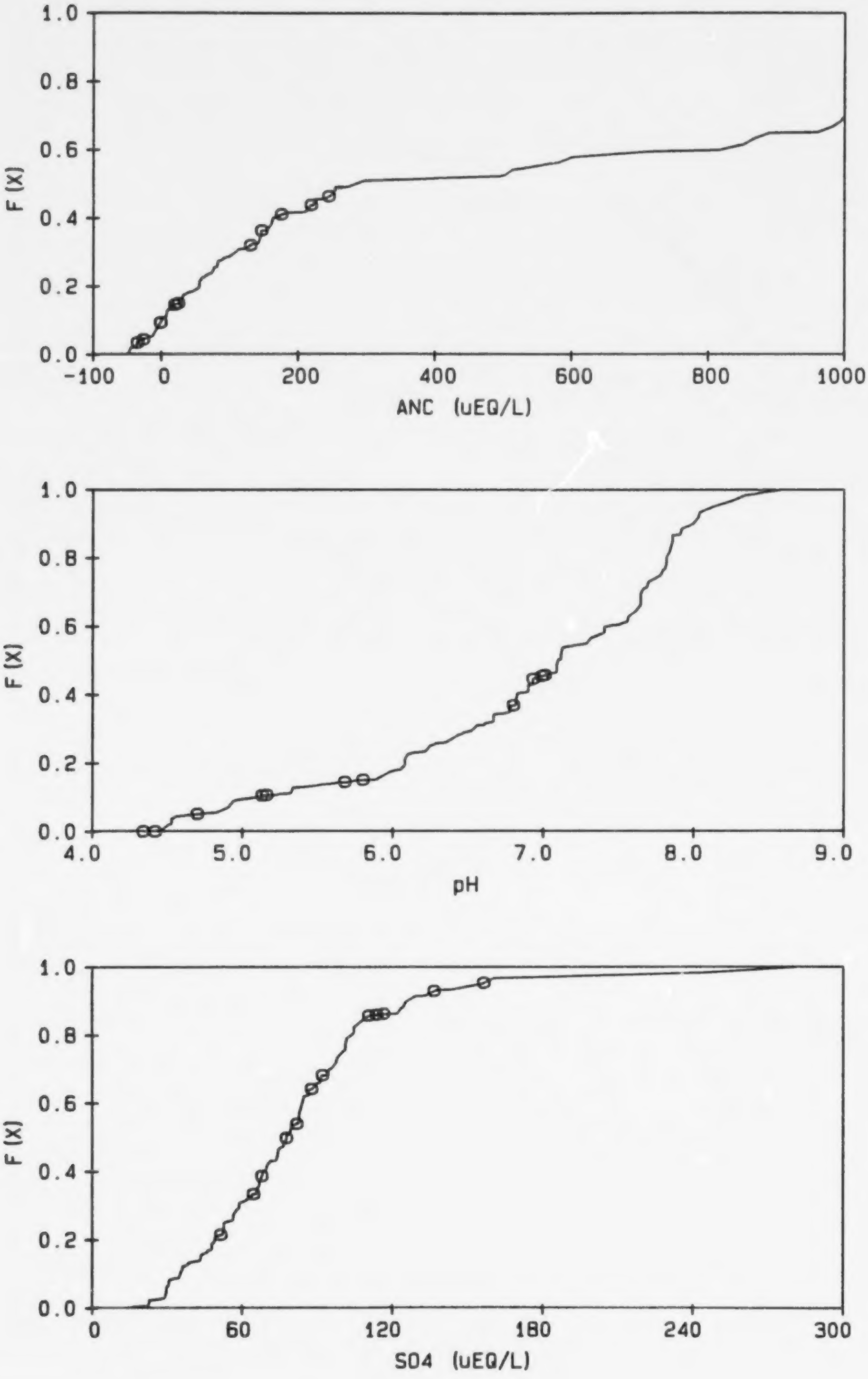
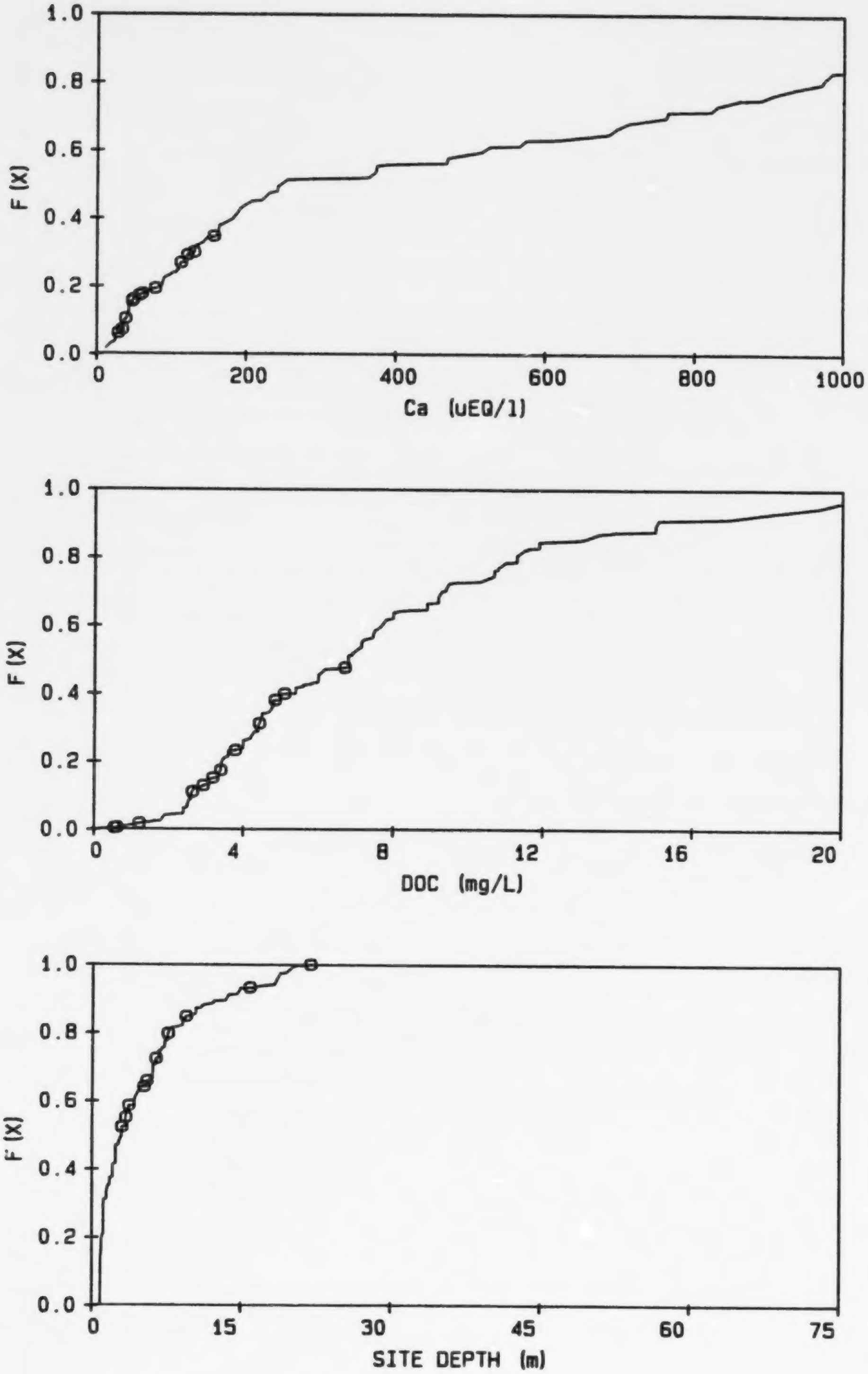
0.8
0.6
0.4
0.2
0.0
0
3000
6000
9000
12000
15000
WATERSHED AREA (ha)
F (X)
1.0
0.8
0.6
0.4
0.2
0.0
0
200
400
600
800
1000
LAKE AREA (ha)
F (X)
1.0
0.8
0.6
0.4
0.2
0.0
0
80
160
240
320
400
WATERSHED AREA : LAKE AREA

2B



F (X)
1.0
0.8
0.6
0.4
0.2
0.0
-100
0
200
400
600
800
1000
ANC (uEQ/L)
F (X)
1.0
0.8
0.6
0.4
0.2
0.0
4.0
5.0
6.0
7.0
8.0
9.0
pH
F (X)
1.0
0.8
0.6
0.4
0.2
0.0
0
60
120
180
240
300
SO4 (uEQ/L)

2B



F(X)
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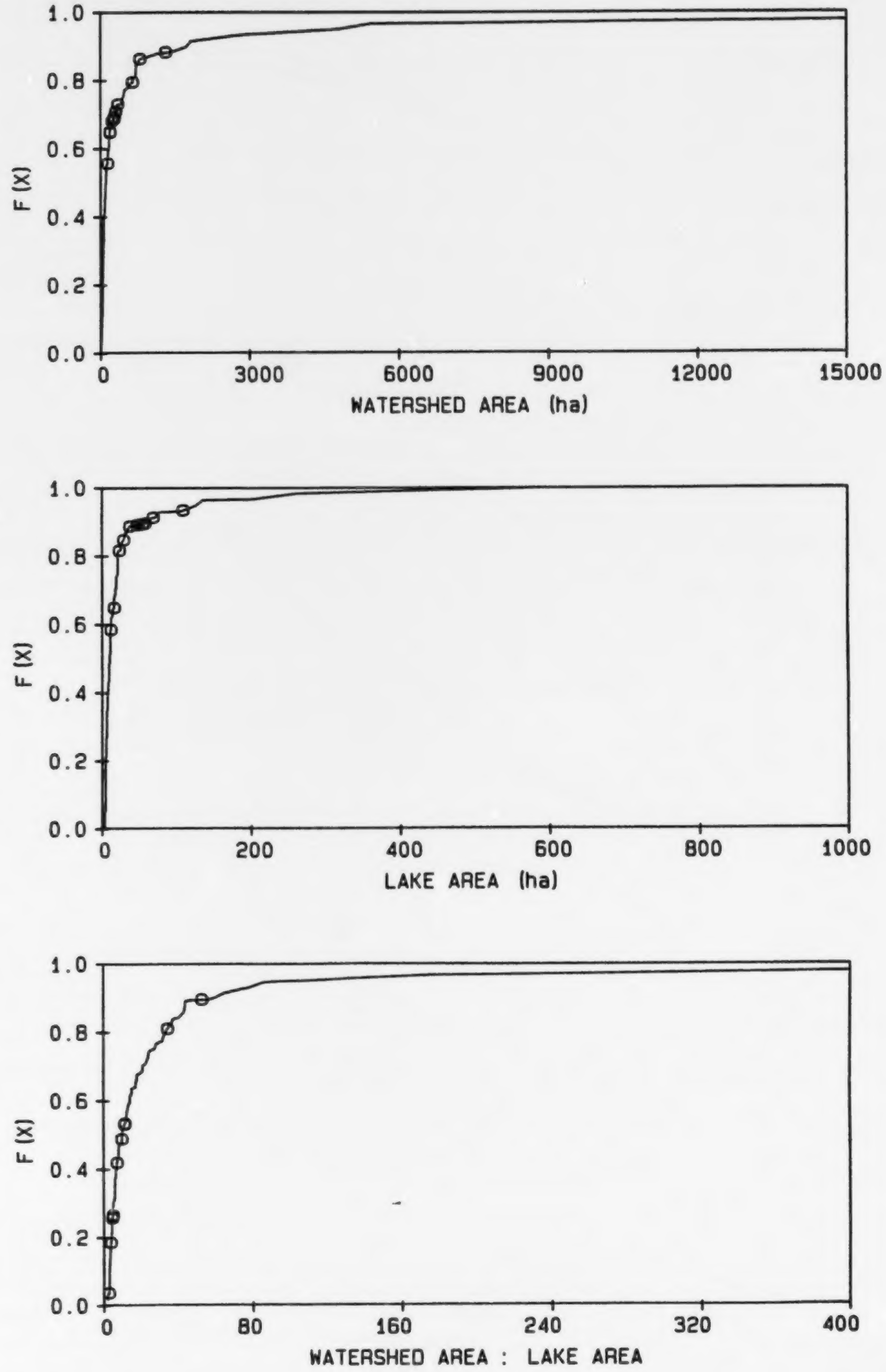
0.6
0.4
0.2
0.0
0
200
400
600
800
1000
Ca (uEQ/l)
F(X)
1.0
0.8
0.6
0.4
0.2
0.0
0
4
8
12
16
20
DOC (mg/L)
F(X)
1.0
0.8
0.6
0.4
0.2
0.0
0
15
30
45
60
75
SITE DEPTH (m)

2B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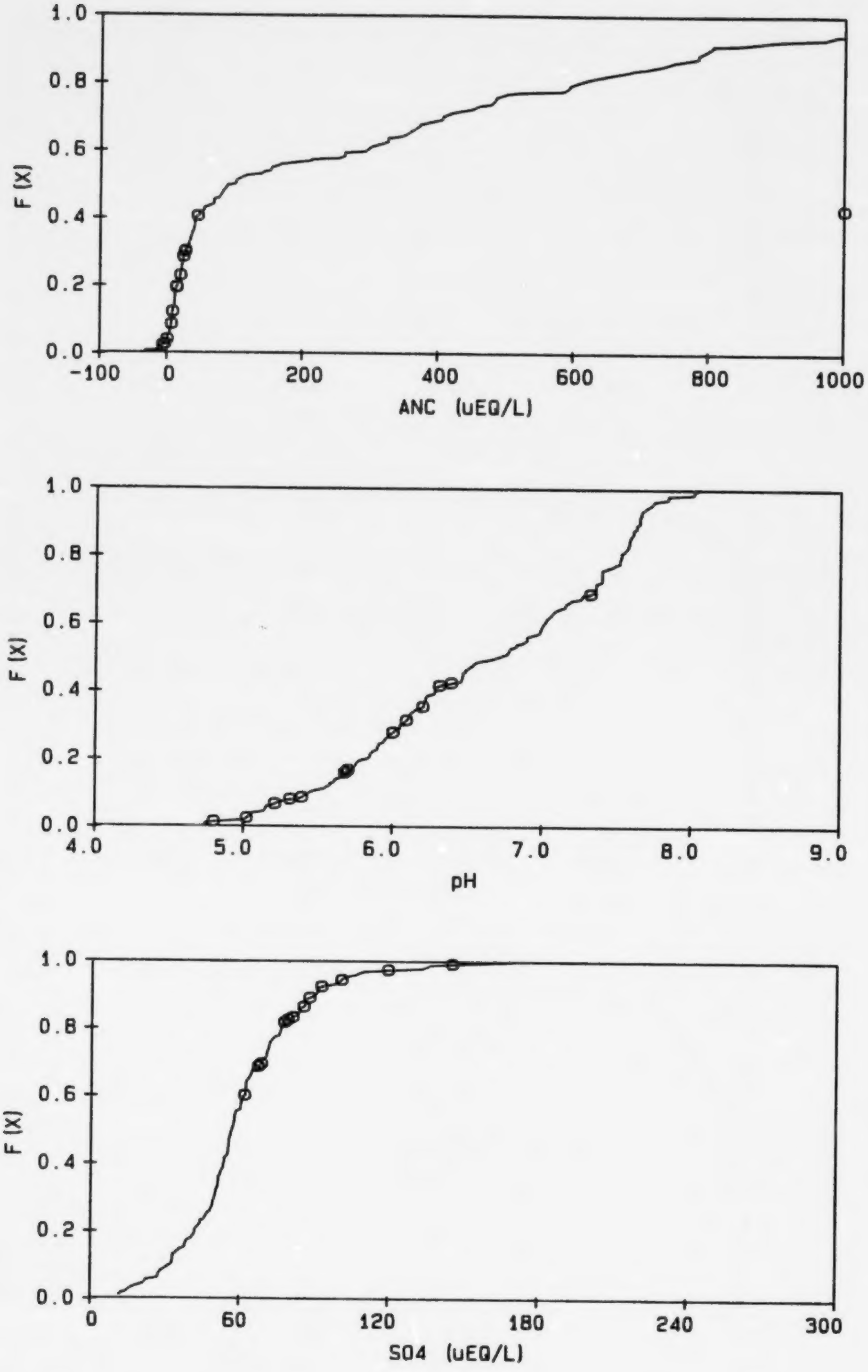
0.8
0.6
0.4
0.2
0.0
0
3000
6000
9000
12000
15000
WATERSHED AREA (ha)
F (X)
1.0
0.8
0.6
0.4
0.2
0.0
0
200
400
600
800
1000
LAKE AREA (ha)
F (X)
1.0
0.8
0.6
0.4
0.2
0.0
0
80
160
240
320
400
WATERSHED AREA : LAKE AREA

2C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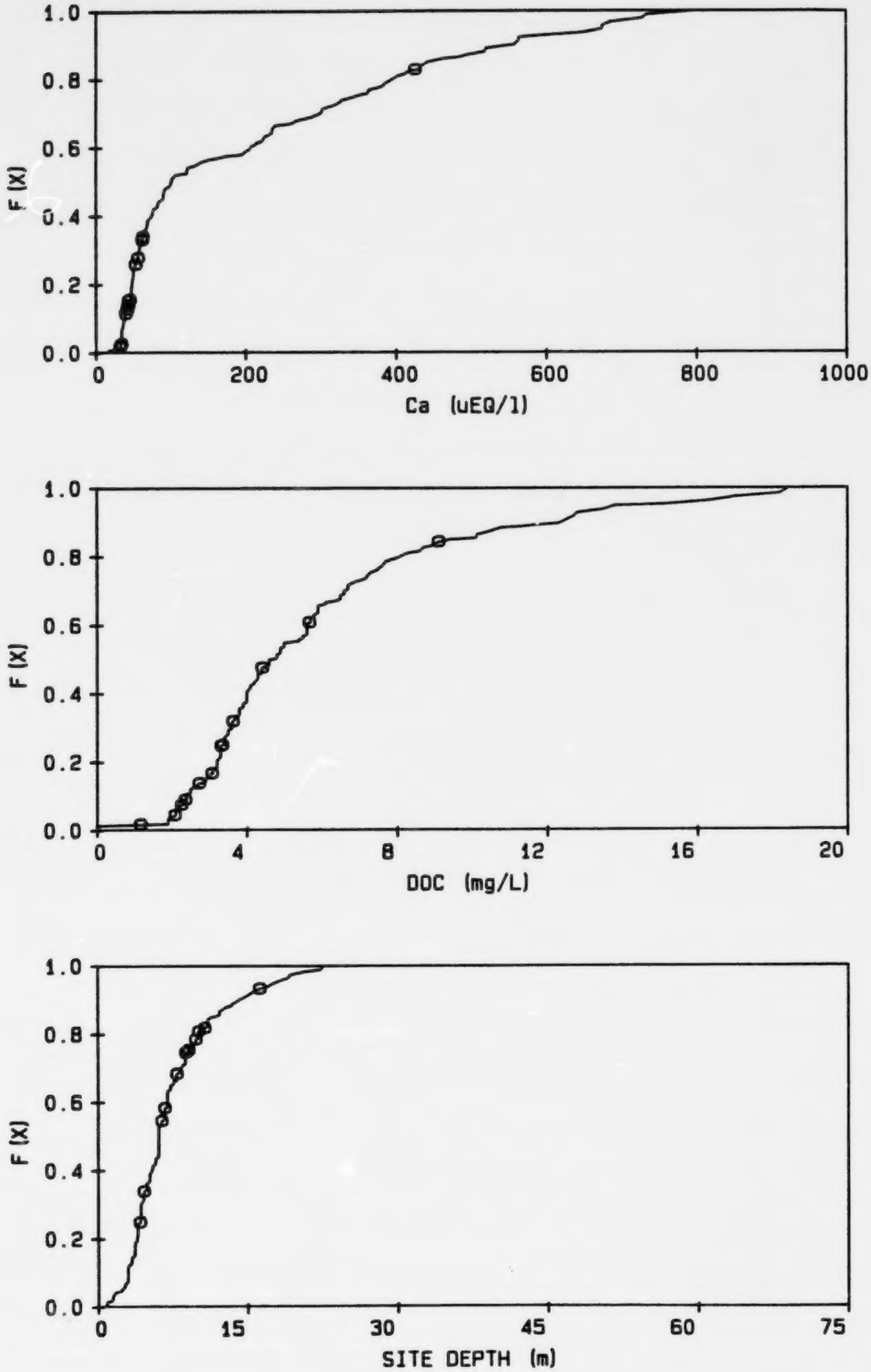
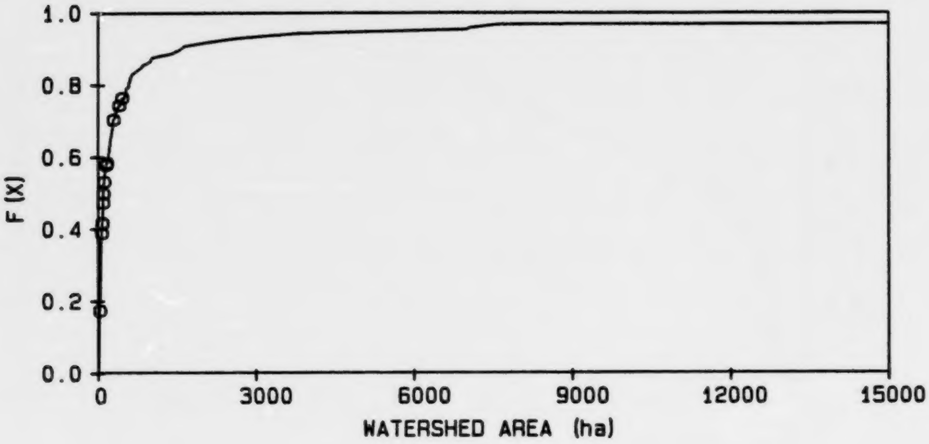
0.8
0.6
0.4
0.2
0.0
-100
0
200
400
600
800
1000
ANC (uEQ/L)
F (X)
1.0
0.8
0.6
0.4
0.2
0.0
4.0
5.0
6.0
7.0
8.0
9.0
pH
F (X)
1.0
0.8
0.6
0.4
0.2
0.0
0
60
120
180
240
300
SO4 (uEQ/L)

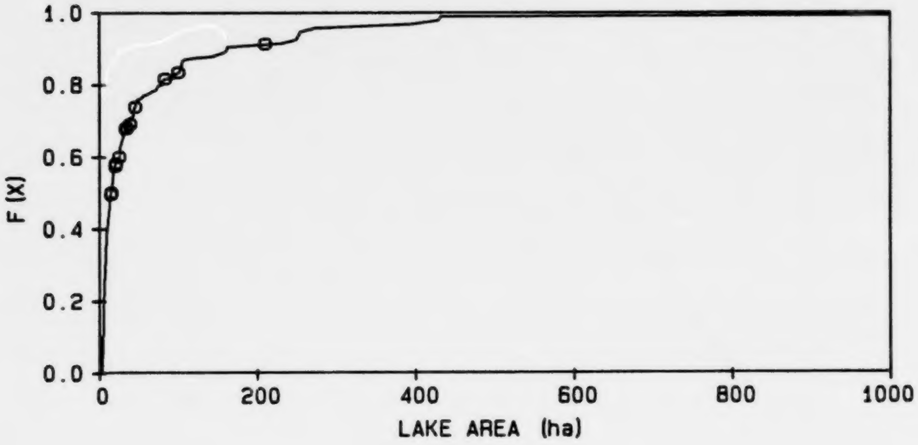
2C


F (X)
1.0
0.8
0.6
0.4
0.2
0.0
0
200
400
600
800
1000
Ca (uEQ/l)
F (X)
1.0
0.8
0.6
0.4
0.2
0.0
0
4
8
12
16
20
DOC (mg/L)
F (X)
1.0
0.8
0.6
0.4
0.2
0.0
0
15
30
45
60
75
SITE DEPTH (m)

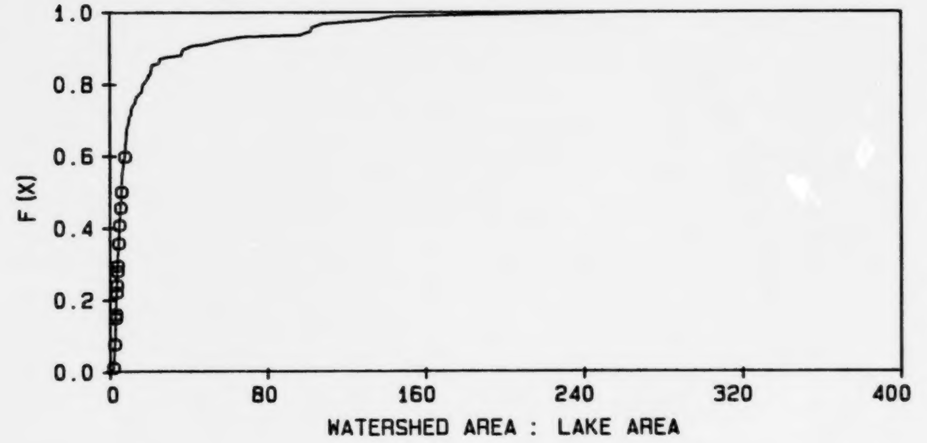
2C



1.0
0.8
0.6
0.4
0.2
0.0
F (X)
0
3000
6000
9000
12000
15000
WATERSHED AREA (ha)

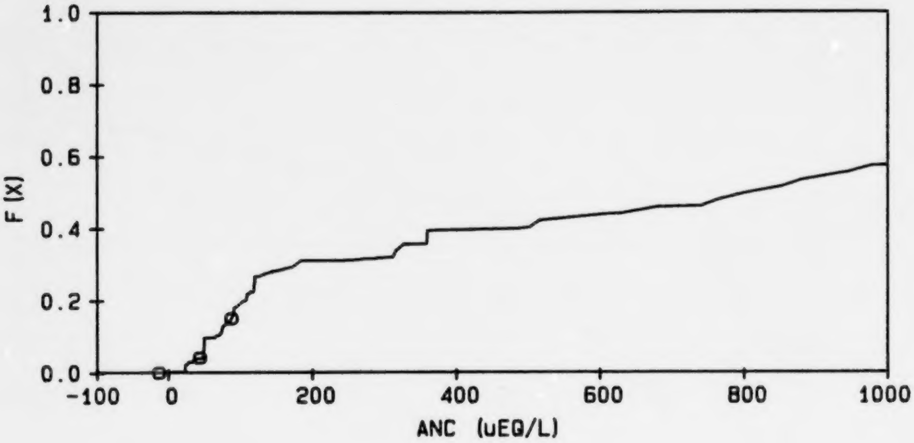


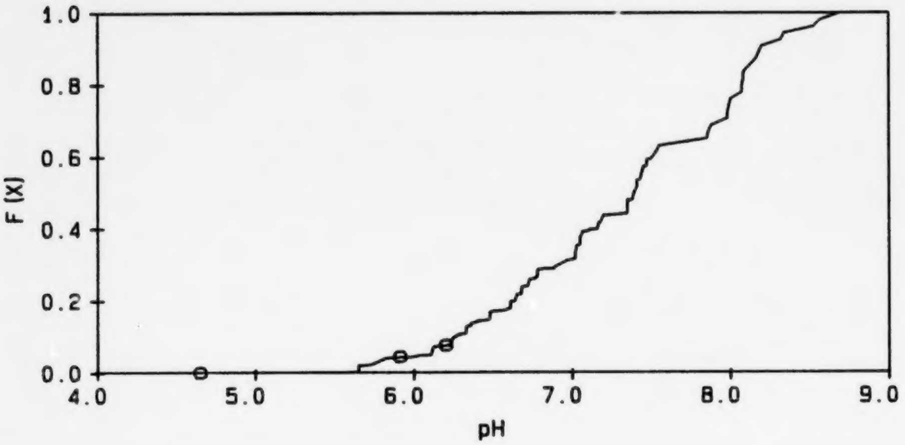
1.0
0.8
0.6
0.4
0.2
0.0
F (X)
0
200
400
600
800
1000
LAKE AREA (ha)

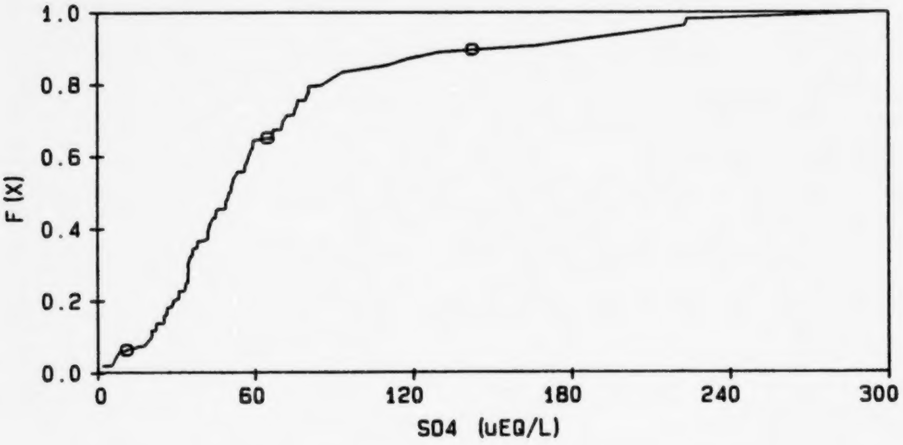


1.0
0.8
0.6
0.4
0.2
0.0
F (X)
0
80
160
240
320
400
WATERSHED AREA : LAKE AREA

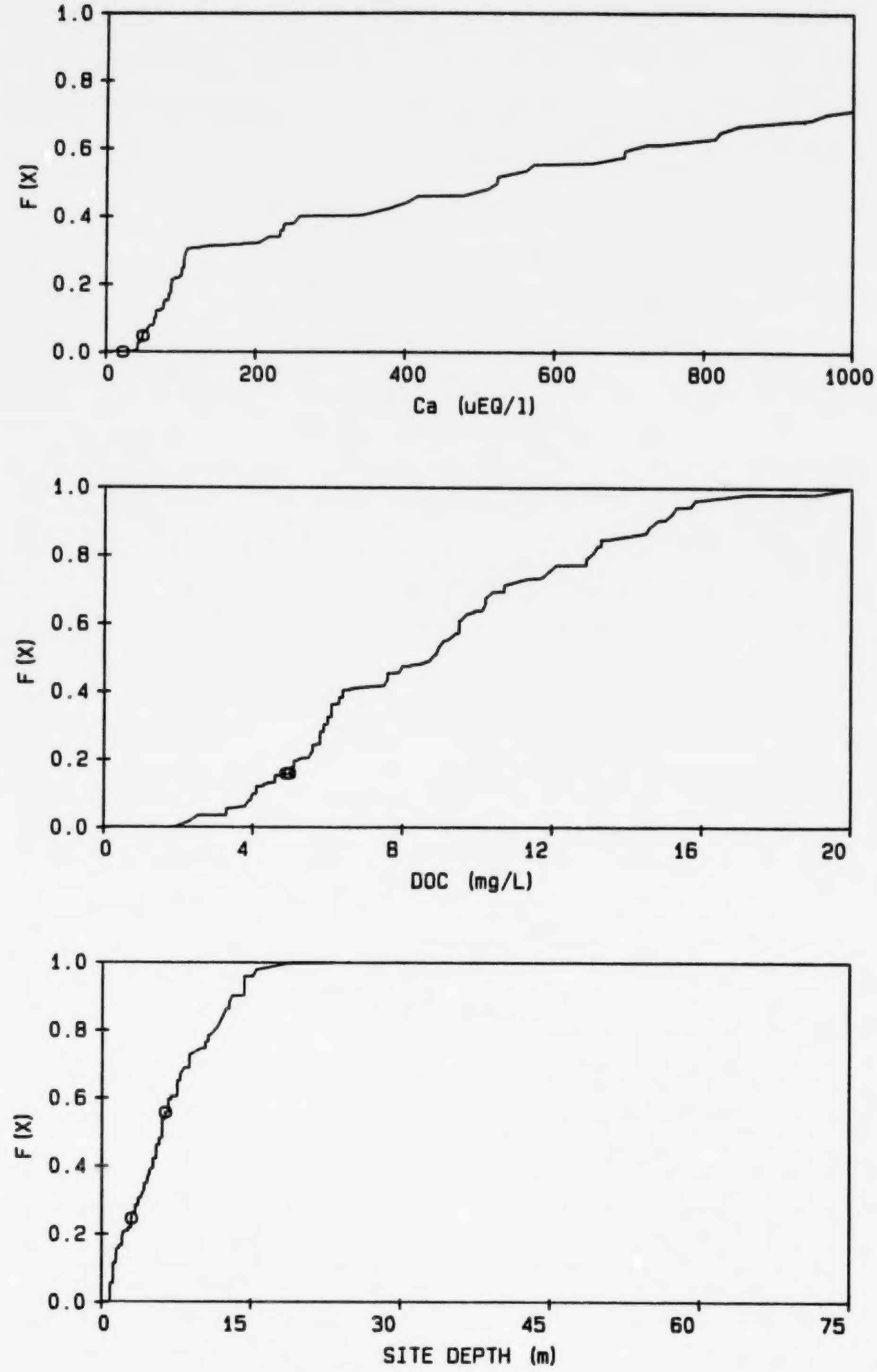
2D


1.0
0.8
0.6
0.4
0.2
0.0
F (X)
-100
0
200
400
600
800
1000
ANC (uEQ/L)

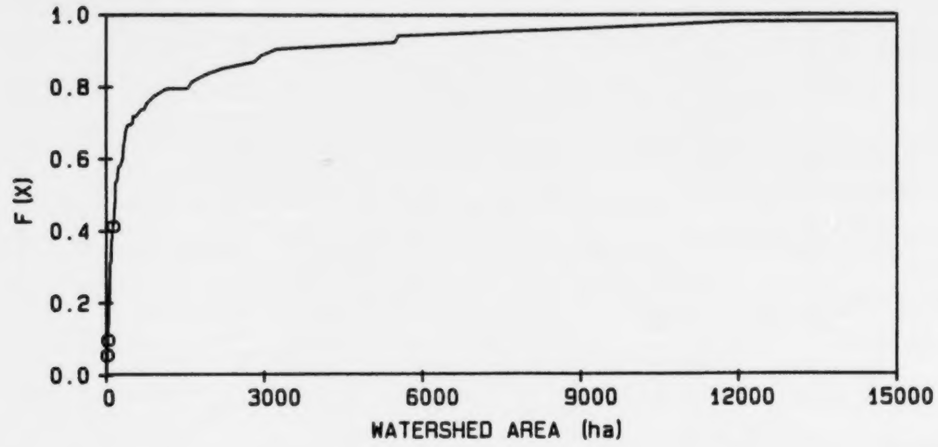

1.0
0.8
0.6
0.4
0.2
0.0
F (X)
4.0
5.0
6.0
7.0
8.0
9.0
pH


1.0
0.8
0.6
0.4
0.2
0.0
F (X)
0
60
120
180
240
300
SO4 (uEQ/L)

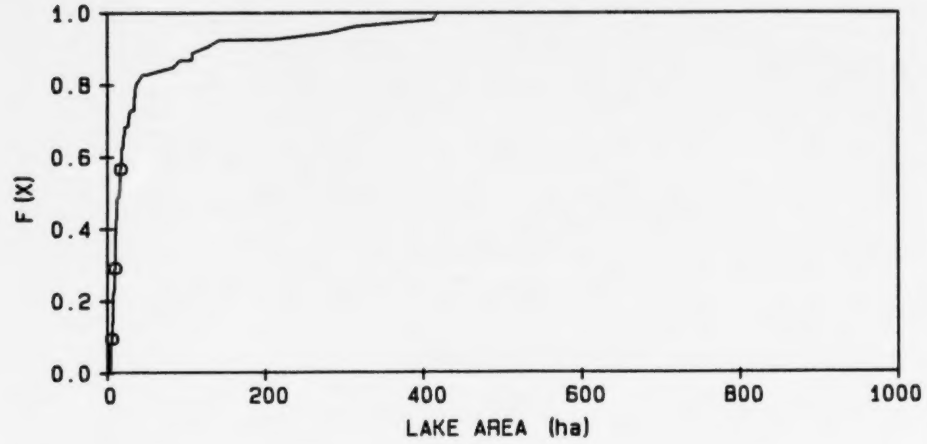
2D


1.0
0.8
0.6
0.4
0.2
0.0
F (X)
0
200
400
600
800
1000
Ca (uEQ/l)
1.0
0.8
0.6
0.4
0.2
0.0
F (X)
0
4
8
12
16
20
DOC (mg/L)
1.0
0.8
0.6
0.4
0.2
0.0
F (X)
0
15
30
45
60
75
SITE DEPTH (m)

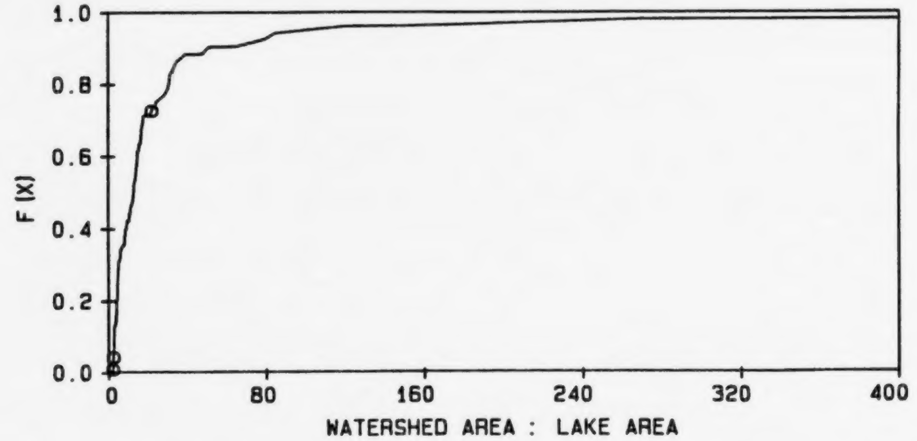
2D



1.0
0.8
0.6
0.4
0.2
0.0
F (X)
0
3000
6000
9000
12000
15000
WATERSHED AREA (ha)

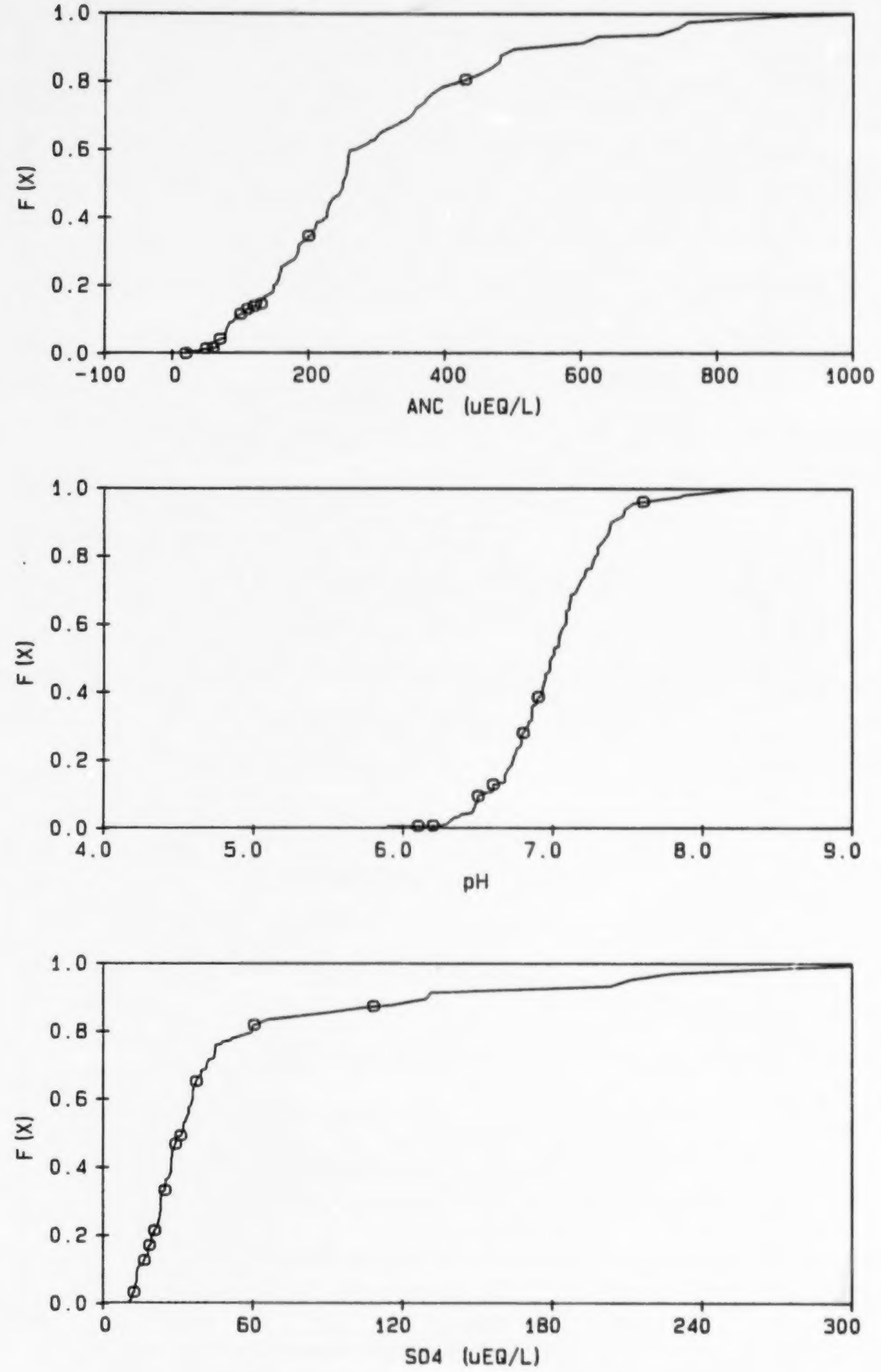


1.0
0.8
0.6
0.4
0.2
0.0
F (X)
0
200
400
600
800
1000
LAKE AREA (ha)

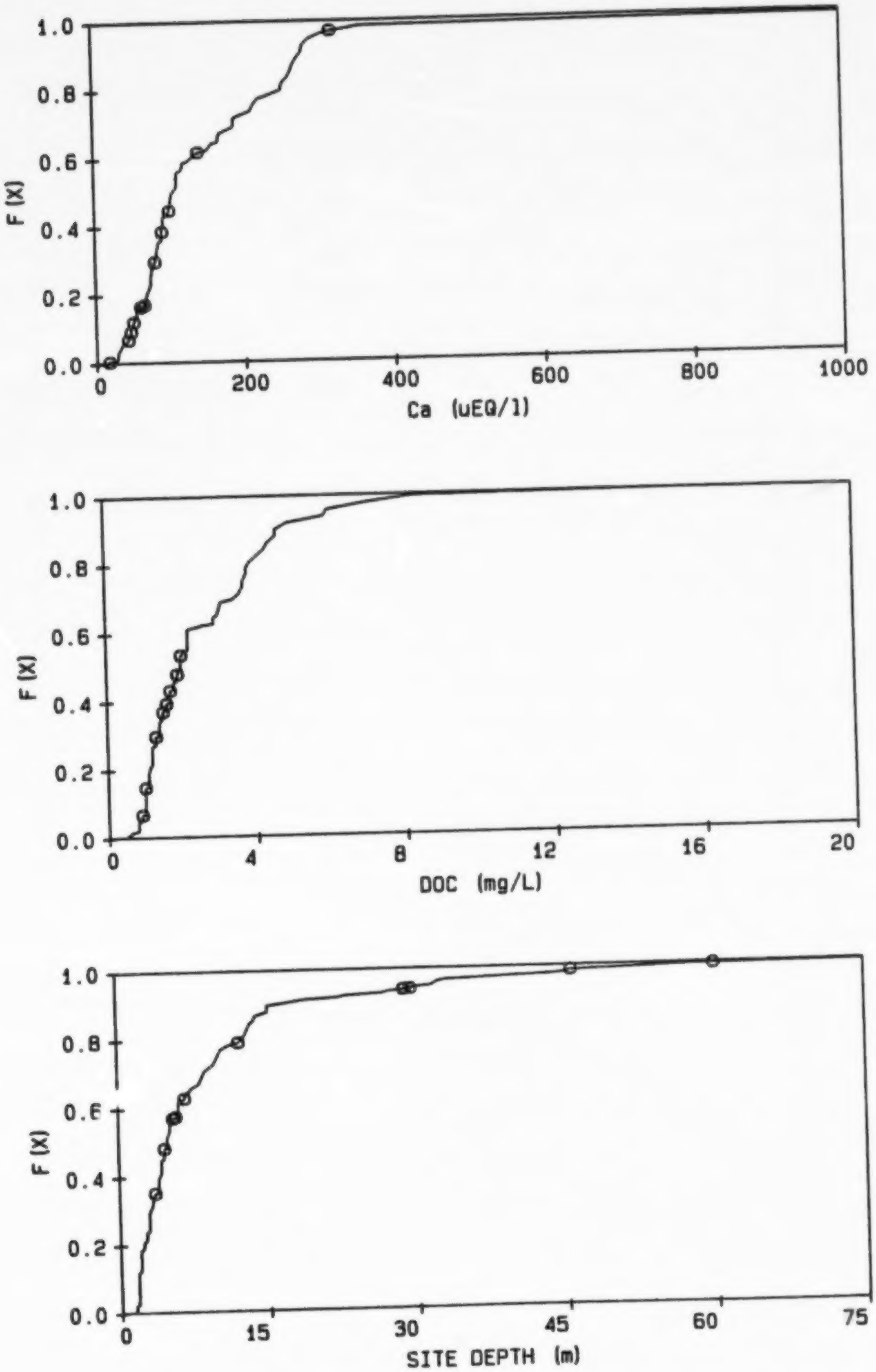


1.0
0.8
0.6
0.4
0.2
0.0
F (X)
0
80
160
240
320
400
WATERSHED AREA : LAKE AREA

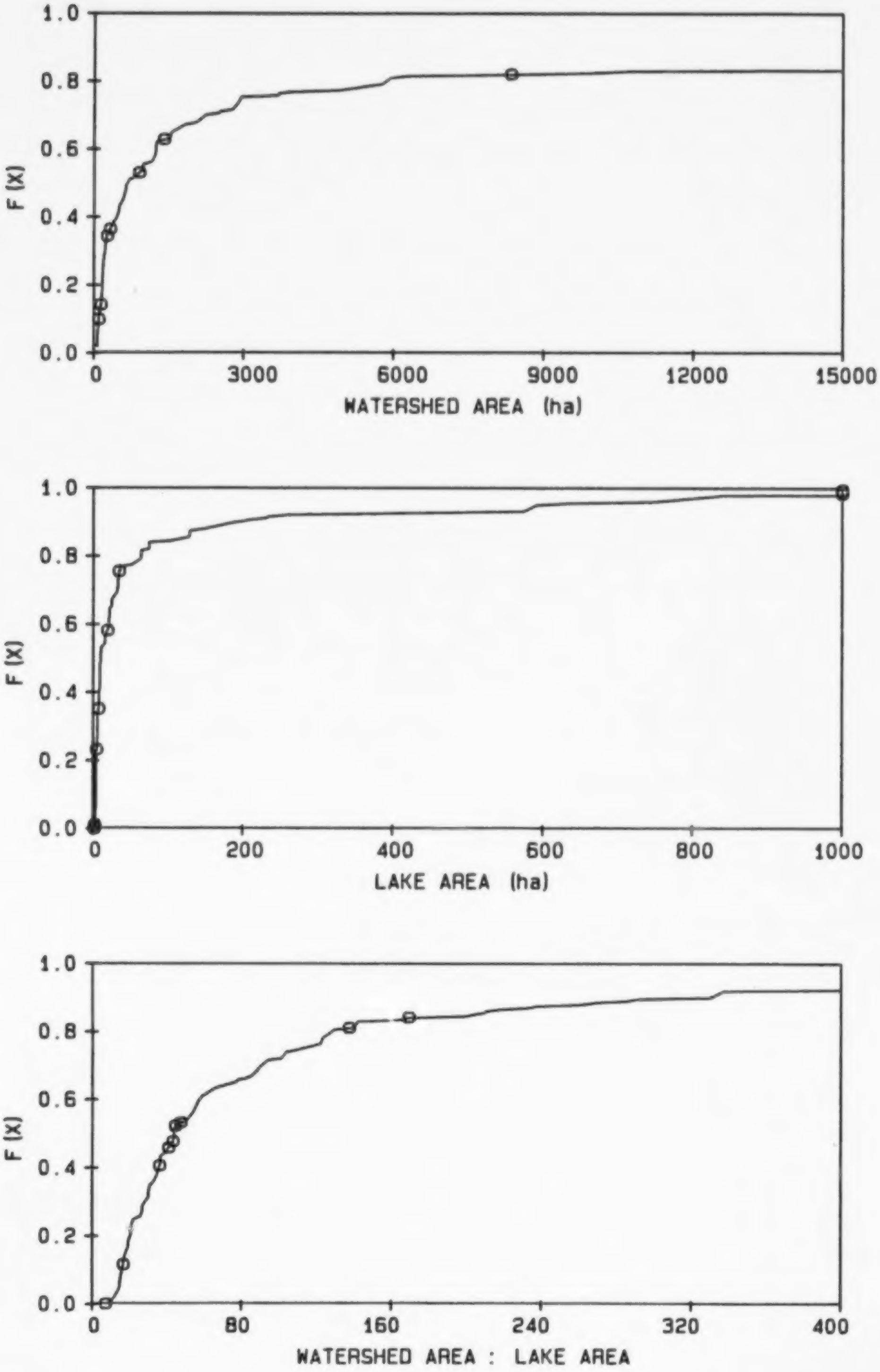
3A


1.0
0.8
0.6
0.4
0.2
0.0
F (X)
-100
0
200
400
600
800
1000
ANC (uEQ/L)
1.0
0.8
0.6
0.4
0.2
0.0
F (X)
4.0
5.0
6.0
7.0
8.0
9.0
pH
1.0
0.8
0.6
0.4
0.2
0.0
F (X)
0
60
120
180
240
300
SO4 (uEQ/L)

3A

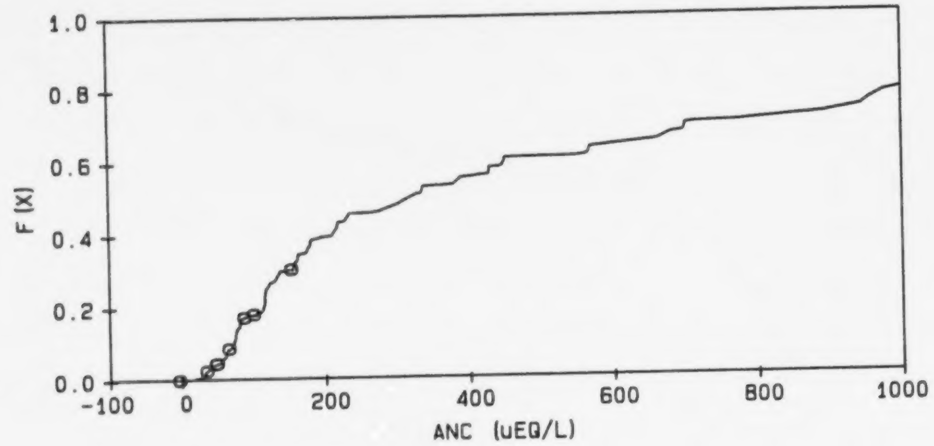

F (X)
1.0
0.8
0.6
0.4
0.2
0.0
0
200
400
600
800
1000
Ca (uEQ/l)
F (X)
1.0
0.8
0.6
0.4
0.2
0.0
0
4
8
12
16
20
DOC (mg/L)
F (X)
1.0
0.8
0.6
0.4
0.2
0.0
0
15
30
45
60
75
SITE DEPTH (m)

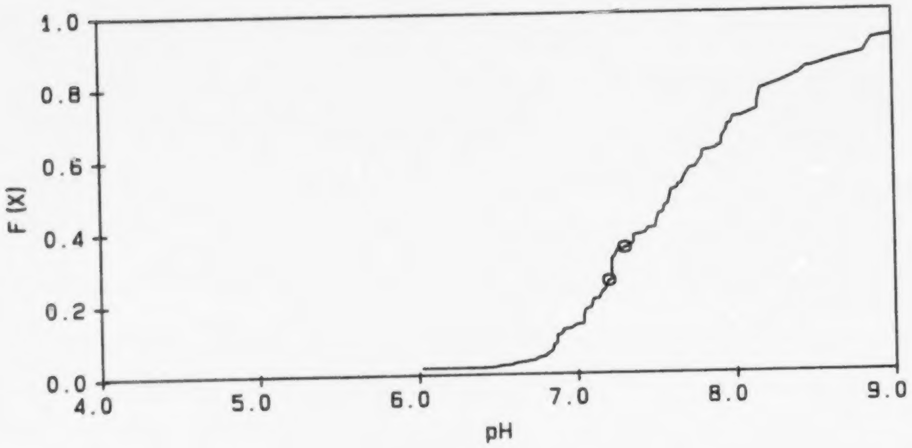
3A

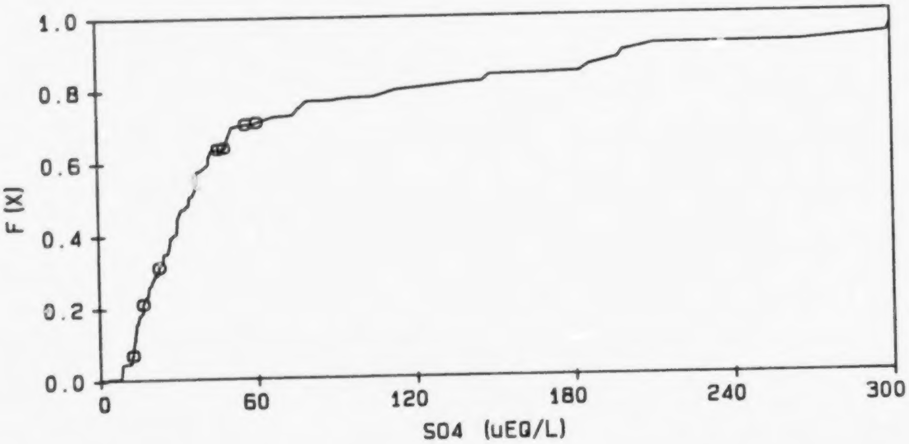


1.0
0.8
0.6
0.4
0.2
0.0
F (X)
0
3000
6000
9000
12000
15000
WATERSHED AREA (ha)
1.0
0.8
0.6
0.4
0.2
0.0
F (X)
0
200
400
600
800
1000
LAKE AREA (ha)
1.0
0.8
0.6
0.4
0.2
0.0
F (X)
0
80
160
240
320
400
WATERSHED AREA : LAKE AREA

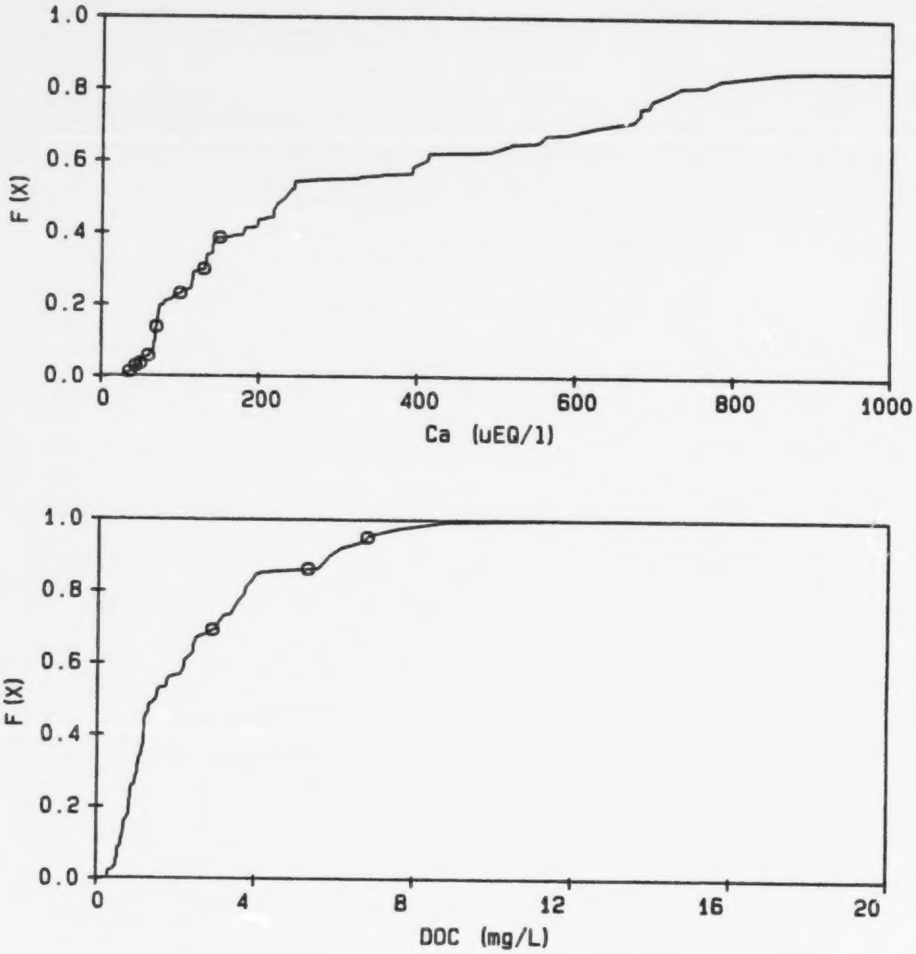
4E


1.0
0.8
0.6
0.4
0.2
0.0
F [X]
-100
0
200
400
600
800
1000
ANC (uEQ/L)


1.0
0.8
0.6
0.4
0.2
0.0
F [X]
4.0
5.0
6.0
7.0
8.0
9.0
pH

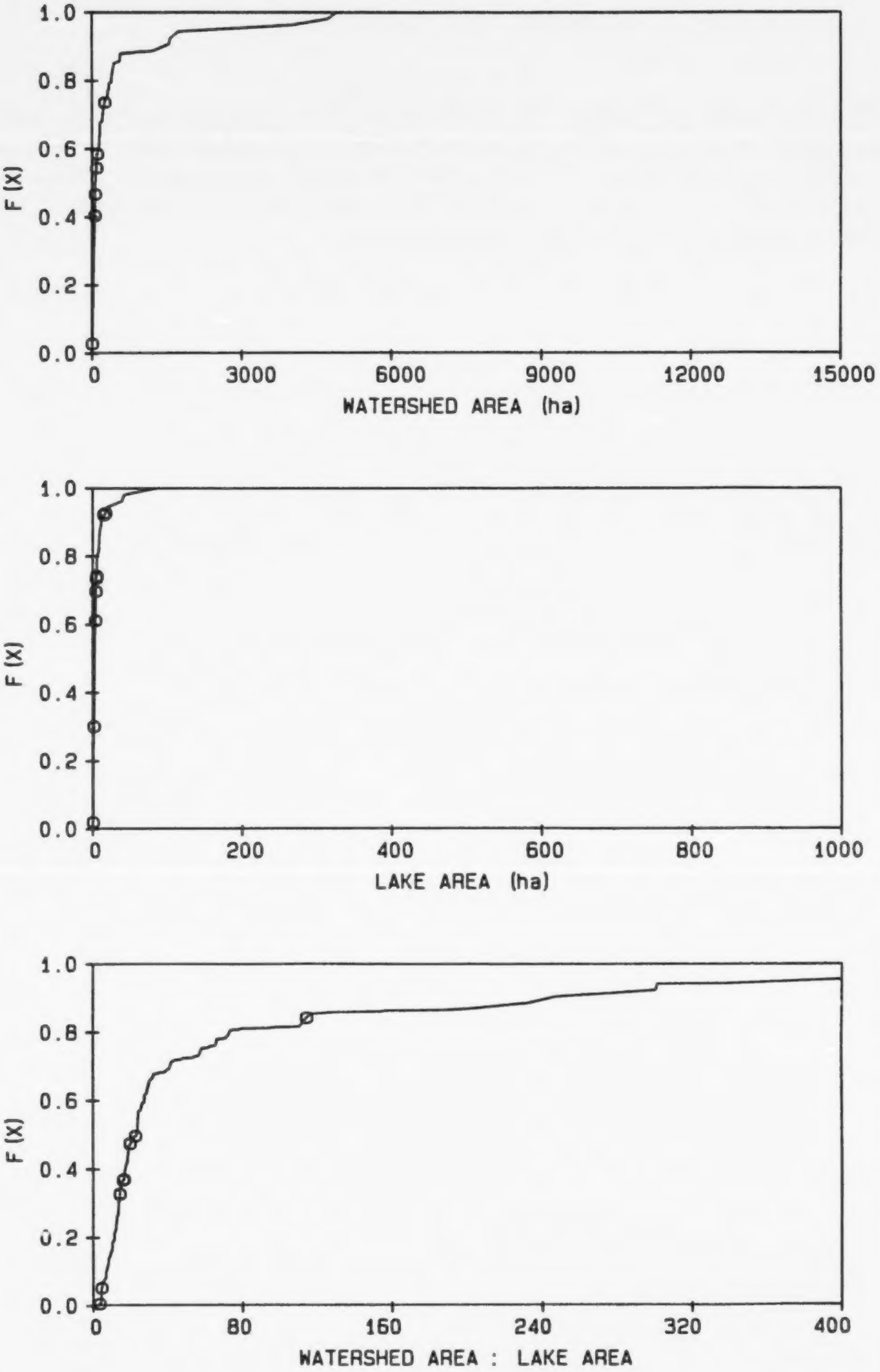

1.0
0.8
0.6
0.4
0.2
0.0
F [X]
0
60
120
180
240
300
SO4 (uEQ/L)

4E



Site depth information not available

4E


1.0
0.8
0.6
0.4
0.2
0.0
F (X)
0
3000
6000
9000
12000
15000
WATERSHED AREA (ha)
1.0
0.8
0.6
0.4
0.2
0.0
F (X)
0
200
400
600
800
1000
LAKE AREA (ha)
1.0
0.8
0.6
0.4
0.2
0.0
F (X)
0
80
160
240
320
400
WATERSHED AREA : LAKE AREA

APPENDIX D
ESTIMATES OF THE NUMBER OF LAKES TO BE SAMPLED IN THE LTM SUBREGIONS

LTM data were used to estimate the number of lakes that should be sampled in a subregion in order to detect a specified change in the regional mean concentration of a specific variable at any given time in the future. Estimates were calculated guarding against various levels of Type I ($1-\alpha$) and Type II ($1-\beta$) errors, and for various levels of change (see Section 2.3.3). This appendix contains the data for all the LTM subregions.

TABLE D-1. ESTIMATES OF THE NUMBER OF LAKES TO BE SAMPLED IN THE ADIRONDACK SUBREGION (NY) FOR VARIOUS LEVELS OF SIGNIFICANCE, POWER, AND CHANGE

CHANGE IN ANC

		7 Lakes with ANC ≤ 20			8 Lakes with $20 <$ ANC ≤ 100		
$1-\alpha$[1]	$1-\beta$[2]	10 μeq L^{-1}	25 μeq L^{-1}	50 μeq L^{-1}	10 μeq L^{-1}	25 μeq L^{-1}	50 μeq L^{-1}
0.95	0.95	144	27	8	104	18	5
0.95	0.90	115	21	7	82	14	4
0.95	0.80	83	15	5	60	10	3
0.95	0.70	63	12	4	45	8	2
0.90	0.95	115	21	7	82	14	4
0.90	0.90	88	16	5	64	11	3
0.90	0.80	61	11	3	44	8	2
0.90	0.70	44	8	3	32	6	2
0.80	0.95	83	15	5	60	10	3
0.80	0.90	61	11	3	44	8	2
0.80	0.80	38	7	2	28	5	1
0.80	0.70	25	5	1	18	3	1

CHANGE IN pH[3]

$1-\alpha$[1]	$1-\beta$[2]	0.2	0.35	0.5	0.2	0.35	0.5
0.95	0.95	66	21	11	52	17	9
0.95	0.90	52	17	9	41	13	7
0.95	0.80	38	12	6	30	10	5
0.95	0.70	29	9	5	23	7	4
0.90	0.95	52	17	9	41	13	7
0.90	0.90	40	13	7	32	10	5
0.90	0.80	28	9	5	22	7	4
0.90	0.70	20	6	3	16	5	3
0.80	0.95	38	12	6	30	10	5
0.80	0.90	28	9	5	22	7	4
0.80	0.80	18	6	3	14	4	2
0.80	0.70	12	4	2	9	3	2

---

[1] $1-\alpha$ is the probability of not making a type I error.
[2] $1-\beta$ is the probability of not making a type II error (power).
[3] pH levels of change are indicated in pH units.

(Continued)

TABLE D-1. ESTIMATES OF THE NUMBER OF LAKES TO BE SAMPLED IN THE ADIRONDACK SUBREGION (NY) FOR VARIOUS LEVELS OF SIGNIFICANCE, POWER, AND CHANGE (Continued)

		7 lakes with ANC ≤ 20			8 Lakes with 20 < ANC ≤ 100		
		% CHANGE IN SO_4^{-2}					
1-α[1]	1-β[2]	10%	25%	50%	10%	25%	50%
0.95	0.95	217	39	12	24	4	1
0.95	0.90	172	31	9	19	3	1
0.95	0.80	125	23	7	14	3	1
0.95	0.70	95	17	5	11	2	1
0.90	0.95	172	31	9	19	3	1
0.90	0.90	133	24	7	15	3	1
0.90	0.80	91	17	5	10	2	1
0.90	0.70	66	12	4	7	1	1
0.80	0.95	125	23	7	14	3	1
0.80	0.90	91	17	5	10	2	1
0.80	0.80	58	10	3	6	1	1
0.80	0.70	38	7	2	4	1	1

[1] 1-α is the probability of not making a type I error.

[2] 1-β is the probability of not making a type II error (power).

TABLE D-2. ESTIMATES OF THE NUMBER OF LAKES TO BE SAMPLED IN THE VERMONT SUBREGION (VT) FOR VARIOUS LEVELS OF SIGNIFICANCE, POWER, AND CHANGE

		11 Lakes with ANC ≤ 20			19 Lakes with 20 < ANC ≤ 100		
		CHANGE IN ANC					
$1-\alpha$[1]	$1-\beta$[2]	10 $\mu eq\ L^{-1}$	25 $\mu eq\ L^{-1}$	50 $\mu eq\ L^{-1}$	10 $\mu eq\ L^{-1}$	25 $\mu eq\ L^{-1}$	50 $\mu eq\ L^{-1}$
0.95	0.95	22	4	1	73	13	4
0.95	0.90	17	3	1	58	10	3
0.95	0.80	13	2	1	42	7	2
0.95	0.70	10	2	1	32	6	2
0.90	0.95	17	3	1	58	10	3
0.90	0.90	13	2	1	45	8	2
0.90	0.80	9	2	1	31	5	2
0.90	0.70	7	1	1	22	4	1
0.80	0.95	13	2	1	42	7	2
0.80	0.90	9	2	1	31	5	2
0.80	0.80	6	1	1	19	3	1
0.80	0.70	4	1	1	13	2	1
		CHANGE IN pH[3]					
$1-\alpha$[1]	$1-\beta$[2]	0.2	0.35	0.5	0.2	0.35	0.5
0.95	0.95	41	13	7	33	11	5
0.95	0.90	33	11	5	26	8	4
0.95	0.80	24	8	4	19	6	3
0.95	0.70	18	6	3	14	5	2
0.90	0.95	33	11	5	26	8	4
0.90	0.90	25	8	4	20	7	3
0.90	0.80	17	6	3	14	4	2
0.90	0.70	13	4	2	10	3	2
0.80	0.95	24	8	4	19	6	3
0.80	0.90	17	6	3	14	4	2
0.80	0.80	11	4	2	9	3	1
0.80	0.70	7	2	1	6	2	1

[1] $1-\alpha$ is the probability of not making a Type I error.
[2] $1-\beta$ is the probability of not making a Type II error (power).
[3] pH levels of change are indicated in pH units.

(Continued)

TABLE D-2. ESTIMATES OF THE NUMBER OF LAKES TO BE SAMPLED IN THE VERMONT SUBREGION (VT) FOR VARIOUS LEVELS OF SIGNIFICANCE, POWER, AND CHANGE (Continued)

		11 Lakes with ANC ≤ 20			19 Lakes with 20 < ANC ≤ 100		
		% CHANGES IN SO_4^{-2}					
1-α[1]	1-β[2]	10 %	25 %	50 %	10 %	25 %	50 %
0.95	0.95	48	9	3	36	7	2
0.95	0.90	38	7	2	29	5	2
0.95	0.80	28	5	2	21	4	1
0.95	0.70	21	4	1	16	3	1
0.95	0.95	38	7	2	29	5	2
0.90	0.90	30	5	2	22	4	1
0.90	0.80	20	4	1	15	3	1
0.90	0.70	15	3	1	11	2	1
0.80	0.95	28	5	2	21	4	1
0.80	0.90	20	4	1	15	3	1
0.80	0.80	13	2	1	10	2	1
0.80	0.70	8	2	1	6	1	1

[1] 1-α is the probability of not making a Type I error.

[2] 1-β is the probability of not making a Type II error (power).

TABLE D-3. ESTIMATES OF THE NUMBER OF LAKES TO BE SAMPLED IN THE MAINE SUBREGION (ME) FOR VARIOUS LEVELS OF SIGNIFICANCE, POWER, AND CHANGE

		4 Lakes with ANC ≤ 20			2 Lakes with 20 < ANC ≤ 100		
		CHANGE IN ANC					
1-α[1]	1-β[2]	10 μeq L^{-1}	25 μeq L^{-1}	50 μeq L^{-1}	10 μeq L^{-1}	25 μeq L^{-1}	50 μeq L^{-1}
0.95	0.95	55	10	3	8	1	1
0.95	0.90	44	8	2	6	1	1
0.95	0.80	32	6	2	4	1	1
0.95	0.70	24	4	1	3	1	1
0.90	0.95	44	8	2	6	1	1
0.90	0.90	34	6	2	5	1	1
0.90	0.80	23	4	1	3	1	1
0.90	0.70	17	3	1	2	1	1
0.80	0.95	32	6	2	4	1	1
0.80	0.90	23	4	1	3	1	1
0.80	0.80	15	3	1	2	1	1
0.80	0.70	10	2	1	1	1	1
		CHANGE IN pH[3]					
1-α[1]	1-β[2]	0.2	0.35	0.5	0.2	0.35	0.5
0.95	0.95	135	44	22	2	1	1
0.95	0.90	107	35	18	2	1	1
0.95	0.80	77	25	13	1	1	1
0.95	0.70	59	19	10	1	1	1
0.90	0.95	107	35	18	2	1	1
0.90	0.90	82	27	14	1	1	1
0.90	0.80	57	18	9	1	1	1
0.90	0.70	41	13	7	1	1	1
0.80	0.95	77	25	13	1	1	1
0.80	0.90	57	18	9	1	1	1
0.80	0.80	36	12	6	1	1	1
0.80	0.70	24	8	4	1	1	1

---

[1] 1-α is the probability of not making a Type I error.

[2] 1-β is the probability of not making a Type II error (power).

[3] pH levels of change are indicated in pH units.

(Continued)

TABLE D-3. ESTIMATES OF THE NUMBER OF LAKES TO BE SAMPLED IN THE MAINE SUBREGION (ME) FOR VARIOUS LEVELS OF SIGNIFICANCE, POWER, AND CHANGE (Continued)

		4 Lakes with ANC $\leq$ 20			2 Lakes with 20 < ANC $\leq$ 100		
		% CHANGES IN SO_4^{-2}					
$1-\alpha$[1]	$1-\beta$[2]	10 %	25 %	50 %	10 %	25 %	50 %
0.95	0.95	72	13	4	4	1	1
0.95	0.90	57	10	3	4	1	1
0.95	0.80	42	8	2	3	1	1
0.95	0.70	32	6	2	2	1	1
0.90	0.95	57	10	3	4	1	1
0.90	0.90	44	8	2	3	1	1
0.90	0.80	30	6	2	2	1	1
0.90	0.70	22	4	1	1	1	1
0.80	0.95	42	8	2	3	1	1
0.80	0.90	30	6	2	2	1	1
0.80	0.80	19	3	1	1	1	1
0.80	0.70	13	2	1	1	1	1

[1] $1-\alpha$ is the probability of not making a Type I error.

[2] $1-\beta$ is the probability of not making a Type II error (power).

TABLE D-4. ESTIMATES OF THE NUMBER OF LAKES TO BE SAMPLED IN THE UPPER MIDWEST REGION (UPMW) FOR VARIOUS LEVELS OF SIGNIFICANCE, POWER, AND CHANGE

		13 Lakes with ANC ≤ 20			8 Lakes with 20 < ANC ≤ 100		
		CHANGE IN ANC					
$1-\alpha$[1]	$1-\beta$[2]	10 μeq L^{-1}	25 μeq L^{-1}	50 μeq L^{-1}	10 μeq L^{-1}	25 μeq L^{-1}	50 μeq L^{-1}
0.95	0.95	119	22	7	128	22	6
0.95	0.90	95	17	5	101	18	5
0.95	0.80	68	13	4	73	13	4
0.95	0.70	52	10	3	56	10	3
0.90	0.95	95	17	5	101	18	5
0.90	0.90	73	13	4	78	14	4
0.90	0.80	50	9	3	54	9	3
0.90	0.70	36	7	2	39	7	2
0.80	0.95	68	13	4	73	13	4
0.80	0.90	50	9	3	54	9	3
0.80	0.80	32	6	2	34	6	2
0.80	0.70	21	4	1	22	4	1
		CHANGE IN pH[3]					
$1-\alpha$[1]	$1-\beta$[2]	0.2	0.35	0.5	0.2	0.35	0.5
0.95	0.95	44	14	7	25	8	4
0.95	0.90	35	11	6	20	6	3
0.95	0.80	25	8	4	14	5	2
0.95	0.70	19	6	3	11	3	2
0.90	0.95	35	11	6	20	6	3
0.90	0.90	27	9	4	15	5	2
0.90	0.80	19	6	3	10	3	2
0.90	0.70	13	4	2	8	2	1
0.80	0.95	25	8	4	14	5	2
0.80	0.90	19	6	3	10	3	2
0.80	0.80	12	4	2	7	2	1
0.80	0.70	8	2	1	4	1	1

[1] $1-\alpha$ is the probability of not making a Type I error.

[2] $1-\beta$ is the probability of not making a Type II error (power).

[3] pH levels of change are indicated in pH units.

(Continued)

TABLE D-4. ESTIMATES OF THE NUMBER OF LAKES TO BE SAMPLED IN THE UPPER MIDWEST REGION (UPMW) FOR VARIOUS LEVELS OF SIGNIFICANCE, POWER, AND CHANGE (Continued)

		13 Lakes with ANC ≤ 20			8 Lakes with 20 < ANC ≤ 100		
		% CHANGES IN SO_4^{-2}					
$1-\alpha$[1]	$1-\beta$[2]	10 %	25 %	50 %	10 %	25 %	50 %
0.95	0.95	97	18	5	121	22	7
0.95	0.90	77	14	4	96	17	5
0.95	0.80	55	10	3	69	13	4
0.95	0.70	42	8	2	53	10	3
0.90	0.95	77	14	4	96	17	5
0.90	0.90	59	11	3	74	13	4
0.90	0.80	41	7	2	51	9	3
0.90	0.70	29	5	2	37	7	2
0.80	0.95	55	10	3	69	13	4
0.80	0.90	41	7	2	51	9	3
0.80	0.80	26	5	1	32	6	2
0.80	0.70	17	3	1	21	4	1

[1] $1-\alpha$ is the probability of not making a Type I error.

[2] $1-\beta$ is the probability of not making a Type II error (power).

TABLE D-5. ESTIMATES OF THE NUMBER OF LAKES TO BE SAMPLED IN THE UPPER PENINSULA OF MICHIGAN SUBREGION (MI) FOR VARIOUS LEVELS OF SIGNIFICANCE, POWER, AND CHANGE

6 Lakes with ANC ≤ 20[1]

CHANGE IN ANC

$1-\alpha$[2]	$1-\beta$[3]	10 μeq L^{-1}	25 μeq L^{-1}	50 μeq L^{-1}
0.95	0.95	675	126	39
0.95	0.90	536	100	31
0.95	0.80	387	72	23
0.95	0.70	294	55	17
0.90	0.95	536	100	31
0.90	0.90	412	77	24
0.90	0.80	284	53	17
0.90	0.70	205	38	12
0.80	0.95	387	72	23
0.80	0.90	284	53	17
0.80	0.80	179	33	10
0.80	0.70	118	22	7

CHANGE IN pH[4]

$1-\alpha$[2]	$1-\beta$[3]	0.2	0.35	0.5
0.95	0.95	137	44	23
0.95	0.90	109	35	18
0.95	0.80	79	26	13
0.95	0.70	60	19	10
0.90	0.95	109	35	18
0.90	0.90	84	27	14
0.90	0.80	58	19	10
0.90	0.70	42	14	7
0.80	0.95	79	26	13
0.80	0.90	58	19	10
0.80	0.80	36	12	6
0.80	0.70	24	8	4

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[1] Only one lake with 20 < ANC ≤ 100 was sampled.

[2] $1-\alpha$ is the probability of not making a Type I error.

[3] $1-\beta$ is the probability of not making a Type II error (power).

[4] pH levels of change are indicated in pH units.

(Continued)

TABLE D-5. ESTIMATES OF THE NUMBER OF LAKES TO BE SAMPLED IN THE UPPER PENINSULA OF MICHIGAN SUBREGION (MI) FOR VARIOUS LEVELS OF SIGNIFICANCE, POWER, AND CHANGE (Continued)

		6 Lakes with ANC ≤ 20[1]		
		% CHANGES IN SO_4^{-2}		
$1-\alpha$[2]	$1-\beta$[3]	10 %	25 %	50 %
0.95	0.95	268	49	15
0.95	0.90	213	39	12
0.95	0.80	154	28	8
0.95	0.70	117	21	6
0.90	0.95	213	39	12
0.90	0.90	164	30	9
0.90	0.80	113	20	6
0.90	0.70	82	15	4
0.80	0.95	154	28	8
0.80	0.90	113	20	6
0.80	0.80	71	13	4
0.80	0.70	47	9	3

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[1] Only one lake with 20 < ANC ≤ 100 was sampled.

[2] $1-\alpha$ is the probability of not making a Type I error.

[3] $1-\beta$ is the probability of not making a Type II error (power).

TABLE D-6. ESTIMATES OF THE NUMBER OF LAKES TO BE SAMPLED IN THE NORTH CENTRAL WISCONSIN SUBREGION (WI) FOR VARIOUS LEVELS OF SIGNIFICANCE, POWER, AND CHANGE

		6 Lakes with ANC ≤ 20			5 Lakes with 20 < ANC ≤ 100		
		CHANGE IN ANC					
1-α[1]	1-β[2]	10 μeq L^{-1}	25 μeq L^{-1}	50 μeq L^{-1}	10 μeq L^{-1}	25 μeq L^{-1}	50 μeq L^{-1}
0.95	0.95	32	6	2	49	9	3
0.95	0.90	26	5	1	39	7	2
0.95	0.80	18	3	1	28	5	1
0.95	0.70	14	3	1	21	4	1
0.90	0.95	26	5	1	39	7	2
0.90	0.90	20	4	1	30	5	2
0.90	0.80	14	2	1	21	4	1
0.90	0.70	10	2	1	15	3	1
0.80	0.95	18	3	1	28	5	1
0.80	0.90	14	2	1	21	4	1
0.80	0.80	9	2	1	13	2	1
0.80	0.70	6	1	1	9	2	1
		CHANGE IN pH[3]					
1-α[1]	1-β[2]	0.2	0.35	0.5	0.2	0.35	0.5
0.95	0.95	61	20	10	84	27	14
0.95	0.90	49	16	8	67	22	11
0.95	0.80	35	11	6	48	16	8
0.95	0.70	27	9	4	37	12	6
0.90	0.95	49	16	8	67	22	11
0.90	0.90	37	12	6	51	17	8
0.90	0.80	26	8	4	35	11	6
0.90	0.70	19	6	3	26	8	4
0.80	0.95	35	11	6	48	16	8
0.80	0.90	26	8	4	35	11	6
0.80	0.80	16	5	3	22	7	4
0.80	0.70	11	3	2	15	5	2

[1] 1-α is the probability of not making a Type I error.
[2] 1-β is the probability of not making a Type II error (power).
[3] pH levels of change are indicated in pH units.

(Continued)

TABLE D-6. ESTIMATES OF THE NUMBER OF LAKES TO BE SAMPLED IN THE NORTH CENTRAL WISCONSIN SUBREGION (WI) FOR VARIOUS LEVELS OF SIGNIFICANCE, POWER, AND CHANGE (Continued)

		6 Lakes with ANC ≤ 20			5 Lakes with 20 < ANC ≤ 100		
		% CHANGE IN SO_4^{-2}					
1-α[1]	1-β[2]	10 %	25 %	50 %	10 %	25 %	50 %
0.95	0.95	235	43	13	201	36	11
0.95	0.90	186	34	10	160	29	9
0.95	0.80	135	24	7	115	21	6
0.95	0.70	102	19	6	88	16	5
0.90	0.95	186	34	10	160	29	9
0.90	0.90	143	26	8	123	22	7
0.90	0.80	99	18	5	85	15	5
0.90	0.70	71	13	4	61	11	3
0.80	0.95	135	24	7	115	21	6
0.80	0.90	99	18	5	85	15	5
0.80	0.80	62	11	3	53	10	3
0.80	0.70	41	7	2	35	6	2

[1] 1-α is the probability of not making a Type I error.

[2] 1-β is the probability of not making a Type II error (power).

TABLE D-7. ESTIMATES OF THE NUMBER OF LAKES TO BE SAMPLED IN THE SOUTHERN BLUE RIDGE SUBREGION (SBR) FOR VARIOUS LEVELS OF SIGNIFICANCE, POWER, AND CHANGE

18 Lakes with 20 < ANC ≤ 100 μeq L^{-1}

CHANGE IN ANC

$1-\alpha$[2]	$1-\beta$[3]	10 μeq L^{-1}	25 μeq L^{-1}	50 μeq L^{-1}
0.95	0.95	72	13	4
0.95	0.90	57	10	3
0.95	0.80	41	7	2
0.95	0.70	32	5	2
0.90	0.95	57	10	3
0.90	0.90	44	8	2
0.90	0.80	30	5	1
0.90	0.70	22	4	1
0.80	0.95	41	7	2
0.80	0.90	30	5	1
0.80	0.80	19	3	1
0.80	0.70	13	2	1

CHANGE IN pH[4]

$1-\alpha$[2]	$1-\beta$[3]	0.2	0.35	0.5
0.95	0.95	36	12	6
0.95	0.90	28	9	5
0.95	0.80	21	7	3
0.95	0.70	16	5	3
0.90	0.95	28	9	5
0.90	0.90	22	7	4
0.90	0.80	15	5	2
0.90	0.70	11	4	2
0.80	0.95	21	7	3
0.80	0.90	15	5	2
0.80	0.80	9	3	2
0.80	0.70	6	2	1

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[1] Only one lake with ANC ≤ 20 was sampled.

[2] $1-\alpha$ is the probability of not making a Type I error.

[3] $1-\beta$ is the probability of not making a Type II error (power).

[4] pH levels of change are indicated in pH units.

(Continued)

TABLE D-7. ESTIMATES OF THE NUMBER OF LAKES TO BE SAMPLED IN THE SOUTHERN BLUE RIDGE SUBREGION (SBR) FOR VARIOUS LEVELS OF SIGNIFICANCE, POWER, AND CHANGE (Continued)

18 Lakes with 20 < ANC ≤ 100 μeq L^{-1}

		% CHANGES IN SO_4^{-2}		
1-α[2]	1-β[3]	10 %	25 %	50 %
0.95	0.95	205	37	11
0.95	0.90	163	30	9
0.95	0.80	118	21	6
0.95	0.70	90	16	5
0.90	0.95	163	30	9
0.90	0.90	125	23	7
0.90	0.80	86	16	5
0.90	0.70	62	11	3
0.80	0.95	118	21	6
0.80	0.90	86	16	5
0.80	0.80	54	10	3
0.80	0.70	36	7	2

[1] Only one lake with ANC ≤ 20 was sampled.

[2] 1-α is the probability of not making a Type I error.

[3] 1-β is the probability of not making a Type II error (power).

APPENDIX E

ESTIMATES FOR DURATION OF MONITORING

The tables in this appendix present estimates of the number of samples that should be taken in the future for various levels of significance ($1-\alpha$) and power ($1-\beta$) in order to detect three levels of change in ANC, pH, and SO_4^{-2}. The number of samples was calculated for each lake within a region; to summarize these data, the 25th (Q_1), 50th (median, M), and 75th (Q_4) percentiles of the subregional distributions for two ANC classes (ANC < 20 μeq L^{-1} and 20 < ANC ≤ 100 μeq L^{-1}) are shown. These numbers refer to the number of samples (n) that should be taken in the future to detect a given level of change, assuming a seasonal sampling schedule. Thus, the number of years of expected monitoring (as shown in Figures 3-10 and 3-11 and discussed in Section 3.4.2) is calculated by dividing n by four. Levels of change chosen for these calculations were:

- 10, 25, and 50 μeq L^{-1} for ANC
- 0.2, 0.35, and 0.5 changes in pH units
- 10%, 25%, and 50% changes in SO_4^{-2} concentration

TABLE E-1. REGIONAL DISTRIBUTIONS OF N, THE NUMBER OF SAMPLES REQUIRED TO DETECT THREE LEVELS OF CHANGE IN ANC IN NEW YORK.

NEW YORK
ANC

7 Lakes with ANC < 20 μeq L^{-1}

		10 μeq L^{-1}			25 μeq L^{-1}			50 μeq L^{-1}		
1-α	1-β	Q_1	M	Q_4	Q_1	M	Q_4	Q_1	M	Q_4
0.95	0.95	131.0	523.0	782.0	24.0	95.0	142.0	7.0	28.0	44.0
0.95	0.90	104.0	415.0	621.0	19.0	75.0	113.0	6.0	23.0	35.0
0.95	0.80	75.0	300.0	449.0	14.0	54.0	81.0	4.0	16.0	25.0
0.95	0.70	57.0	228.0	341.0	10.0	41.0	62.0	3.0	12.0	19.0
0.90	0.95	104.0	415.0	621.0	19.0	75.0	113.0	6.0	23.0	35.0
0.90	0.90	80.0	320.0	478.0	15.0	58.0	87.0	4.0	17.0	27.0
0.90	0.80	55.0	220.0	329.0	10.0	40.0	60.0	3.0	12.0	18.0
0.90	0.70	40.0	159.0	238.0	7.0	29.0	43.0	2.0	9.0	13.0
0.80	0.95	75.0	300.0	449.0	14.0	54.0	81.0	4.0	16.0	25.0
0.80	0.90	55.0	220.0	329.0	10.0	40.0	60.0	3.0	12.0	18.0
0.80	0.80	35.0	139.0	208.0	6.0	25.0	38.0	2.0	8.0	12.0
0.80	0.70	23.0	91.0	137.0	4.0	17.0	25.0	1.0	5.0	8.0

8 Lakes with 20 < ANC ≤ 100 μeq L^{-1}

		10 μeq L^{-1}			25 μeq L^{-1}			50 μeq L^{-1}		
1-α	1-β	Q_1	M	Q_4	Q_1	M	Q_4	Q_1	M	Q_4
0.95	0.95	533.5	1192.0	2133.0	94.0	209.0	379.0	27.5	60.0	111.0
0.95	0.90	423.5	946.0	1693.0	75.0	165.5	300.5	21.5	47.5	88.0
0.95	0.80	306.5	684.0	1224.0	54.0	120.0	217.5	15.5	34.5	64.0
0.95	0.70	233.0	520.0	931.0	41.5	91.0	165.5	12.0	26.5	48.5
0.90	0.95	423.5	946.0	1693.0	75.0	165.5	300.5	21.5	47.5	88.0
0.90	0.90	326.0	728.0	1304.0	57.5	127.5	231.5	16.5	36.5	67.5
0.90	0.80	224.5	501.5	897.0	39.5	87.5	159.0	11.0	25.5	46.5
0.90	0.70	162.0	362.5	649.0	29.0	63.5	115.5	8.5	18.5	33.5
0.80	0.95	306.5	684.0	1224.0	54.0	120.0	217.5	15.5	34.5	64.0
0.80	0.90	224.5	501.5	897.0	39.5	87.5	159.0	11.0	25.5	46.5
0.80	0.80	141.5	316.0	566.0	25.0	55.5	100.5	7.0	15.5	29.5
0.80	0.70	93.0	208.5	373.0	16.5	36.5	66.5	4.5	10.5	19.5

TABLE E-2. REGIONAL DISTRIBUTIONS OF N, THE NUMBER OF SAMPLES REQUIRED TO DETECT THREE LEVELS OF CHANGE IN pH IN NEW YORK.

NEW YORK
pH

7 Lakes with ANC < 20 μeq L^{-1}

		0.20 pH units			0.35 pH units			0.50 pH units		
1-α	1-β	Q_1	M	Q_4	Q_1	M	Q_4	Q_1	M	Q_4
0.95	0.95	14.0	300.0	823.0	4.0	97.0	266.0	2.0	49.0	136.0
0.95	0.90	11.0	238.0	653.0	3.0	77.0	211.0	2.0	39.0	108.0
0.95	0.80	8.0	172.0	472.0	3.0	56.0	153.0	1.0	28.0	78.0
0.95	0.70	6.0	131.0	359.0	2.0	42.0	116.0	1.0	22.0	59.0
0.90	0.95	11.0	238.0	653.0	3.0	77.0	211.0	2.0	39.0	108.0
0.90	0.90	8.0	183.0	503.0	3.0	59.0	163.0	1.0	30.0	83.0
0.90	0.80	6.0	126.0	346.0	2.0	41.0	112.0	1.0	21.0	57.0
0.90	0.70	4.0	91.0	250.0	1.0	30.0	81.0	1.0	15.0	41.0
0.80	0.95	8.0	172.0	472.0	3.0	56.0	153.0	1.0	28.0	78.0
0.80	0.90	6.0	126.0	346.0	2.0	41.0	112.0	1.0	21.0	57.0
0.80	0.80	4.0	80.0	218.0	1.0	26.0	71.0	1.0	13.0	36.0
0.80	0.70	2.0	52.0	144.0	1.0	17.0	47.0	0.0	9.0	24.0

8 Lakes with 20 < ANC ≤ 100 μeq L^{-1}

		0.20 pH units			0.35 pH units			0.50 pH units		
1-α	1-β	Q_1	M	Q_4	Q_1	M	Q_4	Q_1	M	Q_4
0.95	0.95	375.5	580.0	857.5	121.5	187.0	277.5	62.0	95.5	141.0
0.95	0.90	298.0	460.0	681.0	96.5	149.0	220.0	49.0	76.0	112.0
0.95	0.80	215.5	332.5	492.0	69.5	107.5	159.0	35.5	55.0	81.5
0.95	0.70	164.0	253.0	374.5	53.0	81.5	121.0	27.0	41.5	62.0
0.90	0.95	298.0	460.0	681.0	96.5	149.0	220.0	49.0	76.0	112.0
0.90	0.90	229.5	354.0	524.0	74.5	114.5	169.5	37.5	58.5	86.5
0.90	0.80	158.0	244.0	360.5	51.0	79.0	116.5	26.0	40.0	59.5
0.90	0.70	114.0	176.5	261.0	37.0	57.0	84.5	19.0	29.5	43.0
0.80	0.95	215.5	332.5	492.0	69.5	107.5	159.0	35.5	55.0	81.5
0.80	0.90	158.0	244.0	360.5	51.0	79.0	116.5	26.0	40.0	59.5
0.80	0.80	99.5	154.0	227.5	32.0	49.5	73.5	16.5	25.5	37.5
0.80	0.70	65.5	101.5	150.0	21.0	33.0	48.5	10.5	17.0	25.0

TABLE E-3. REGIONAL DISTRIBUTIONS OF N, THE NUMBER OF SAMPLES REQUIRED TO DETECT THREE LEVELS OF CHANGE IN SO_4^{-2} IN NEW YORK.

NEW YORK
SO_4^{-2} μeq L^{-1}

7 Lakes with ANC < 20 μeq L^{-1}

		10%			25%			50%		
1-α	1-β	Q_1	M	Q_4	Q_1	M	Q_4	Q_1	M	Q_4
0.95	0.95	80.0	235.0	521.0	14.0	43.0	95.0	4.0	13.0	29.0
0.95	0.90	63.0	187.0	414.0	11.0	34.0	75.0	3.0	10.0	23.0
0.95	0.80	46.0	135.0	299.0	8.0	24.0	54.0	3.0	7.0	16.0
0.95	0.70	35.0	103.0	227.0	6.0	19.0	41.0	2.0	6.0	12.0
0.90	0.95	63.0	187.0	414.0	11.0	34.0	75.0	3.0	10.0	23.0
0.90	0.90	49.0	144.0	319.0	9.0	26.0	58.0	3.0	8.0	17.0
0.90	0.80	34.0	99.0	219.0	6.0	18.0	40.0	2.0	5.0	12.0
0.90	0.70	24.0	71.0	159.0	4.0	13.0	29.0	1.0	4.0	9.0
0.80	0.95	46.0	135.0	299.0	8.0	24.0	54.0	3.0	7.0	16.0
0.80	0.90	34.0	99.0	219.0	6.0	18.0	40.0	2.0	5.0	12.0
0.80	0.80	21.0	62.0	138.0	4.0	11.0	25.0	1.0	3.0	8.0
0.80	0.70	14.0	41.0	91.0	3.0	7.0	17.0	1.0	2.0	5.0

8 Lakes with 20 < ANC ≤ 100 μeq L^{-1}

		10%			25%			50%		
1-α	1-β	Q_1	M	Q_4	Q_1	M	Q_4	Q_1	M	Q_4
0.95	0.95	82.0	122.5	219.5	15.0	22.0	40.0	4.5	6.5	12.0
0.95	0.90	65.0	97.0	174.5	11.5	17.5	32.0	3.5	5.5	9.5
0.95	0.80	47.0	70.5	126.0	8.5	13.0	23.0	2.5	4.0	7.0
0.95	0.70	35.5	53.5	95.5	6.5	10.0	17.5	2.0	3.0	5.5
0.90	0.95	65.0	97.0	174.5	11.5	17.5	32.0	3.5	5.5	9.5
0.90	0.90	50.0	75.0	134.0	9.5	13.5	24.0	3.0	4.0	7.0
0.90	0.80	34.5	51.5	92.0	6.5	9.5	17.0	2.0	3.0	5.0
0.90	0.70	25.0	37.5	66.5	4.5	6.5	12.5	1.0	2.0	3.5
0.80	0.95	47.0	70.5	126.0	8.5	13.0	23.0	2.5	4.0	7.0
0.80	0.90	34.5	51.5	92.0	6.5	9.5	17.0	2.0	3.0	5.0
0.80	0.80	22.0	33.0	58.5	4.0	5.5	10.5	1.0	2.0	3.5
0.80	0.70	14.5	21.0	38.0	2.5	4.0	7.0	1.0	1.0	2.0

TABLE E-4. REGIONAL DISTRIBUTIONS OF N, THE NUMBER OF SAMPLES REQUIRED TO DETECT THREE LEVELS OF CHANGE IN ANC IN VERMONT.

VERMONT
ANC

11 Lakes with ANC < 20 μeq L^{-1}

		10 μeq L^{-1}			25 μeq L^{-1}			50 μeq L^{-1}		
1-α	1-β	Q_1	M	Q_4	Q_1	M	Q_4	Q_1	M	Q_4
0.95	0.95	48.0	87.0	218.0	9.0	16.0	40.0	3.0	5.0	12.0
0.95	0.90	38.0	69.0	173.0	7.0	13.0	31.0	2.0	4.0	9.0
0.95	0.80	28.0	50.0	125.0	5.0	9.0	23.0	2.0	3.0	7.0
0.95	0.70	21.0	38.0	95.0	4.0	7.0	17.0	1.0	2.0	5.0
0.90	0.95	38.0	69.0	173.0	7.0	13.0	31.0	2.0	4.0	9.0
0.90	0.90	30.0	53.0	133.0	6.0	10.0	24.0	2.0	3.0	7.0
0.90	0.80	20.0	37.0	92.0	4.0	7.0	17.0	1.0	2.0	5.0
0.90	0.70	15.0	26.0	66.0	3.0	5.0	12.0	1.0	2.0	4.0
0.80	0.95	28.0	50.0	125.0	5.0	9.0	23.0	2.0	3.0	7.0
0.80	0.90	20.0	37.0	92.0	4.0	7.0	17.0	1.0	2.0	5.0
0.80	0.80	13.0	23.0	58.0	2.0	4.0	10.0	1.0	1.0	3.0
0.80	0.70	8.0	15.0	38.0	2.0	3.0	7.0	0.0	1.0	2.0

19 Lakes with 20 < ANC ≤ 100 μeq L^{-1}

		10 μeq L^{-1}			25 μeq L^{-1}			50 μeq L^{-1}		
1-α	1-β	Q_1	M	Q_4	Q_1	M	Q_4	Q_1	M	Q_4
0.95	0.95	126.0	375.0	662.0	22.0	65.0	116.0	7.0	19.0	34.0
0.95	0.90	100.0	297.0	525.0	18.0	52.0	92.0	5.0	15.0	27.0
0.95	0.80	72.0	215.0	380.0	13.0	38.0	67.0	4.0	11.0	19.0
0.95	0.70	55.0	164.0	289.0	10.0	29.0	51.0	3.0	8.0	15.0
0.90	0.95	100.0	297.0	525.0	18.0	52.0	92.0	5.0	15.0	27.0
0.90	0.90	77.0	229.0	405.0	14.0	40.0	71.0	4.0	11.0	21.0
0.90	0.80	53.0	158.0	278.0	9.0	28.0	49.0	3.0	8.0	14.0
0.90	0.70	38.0	114.0	201.0	7.0	20.0	35.0	2.0	6.0	10.0
0.80	0.95	72.0	215.0	380.0	13.0	38.0	67.0	4.0	11.0	19.0
0.80	0.90	53.0	158.0	278.0	9.0	28.0	49.0	3.0	8.0	14.0
0.80	0.80	33.0	99.0	176.0	6.0	17.0	31.0	2.0	5.0	9.0
0.80	0.70	22.0	66.0	116.0	4.0	11.0	20.0	1.0	3.0	6.0

TABLE E-5. REGIONAL DISTRIBUTIONS OF N, THE NUMBER OF SAMPLES REQUIRED TO DETECT THREE LEVELS OF CHANGE IN pH IN VERMONT.

VERMONT
pH

11 Lakes with ANC < 20 μeq L^{-1}

		0.20 pH units			0.35 pH units			0.50 pH units		
1-α	1-β	Q_1	M	Q_4	Q_1	M	Q_4	Q_1	M	Q_4
0.95	0.95	135.0	166.0	287.0	44.0	54.0	93.0	22.0	27.0	47.0
0.95	0.90	107.0	131.0	228.0	35.0	42.0	74.0	18.0	22.0	38.0
0.95	0.80	77.0	95.0	165.0	25.0	31.0	53.0	13.0	16.0	27.0
0.95	0.70	59.0	72.0	125.0	19.0	23.0	40.0	10.0	12.0	21.0
0.90	0.95	107.0	131.0	228.0	35.0	42.0	74.0	18.0	22.0	38.0
0.90	0.90	82.0	101.0	175.0	27.0	33.0	57.0	14.0	17.0	29.0
0.90	0.80	57.0	70.0	121.0	18.0	23.0	39.0	9.0	11.0	20.0
0.90	0.70	41.0	50.0	87.0	13.0	16.0	28.0	7.0	8.0	14.0
0.80	0.95	77.0	95.0	165.0	25.0	31.0	53.0	13.0	16.0	27.0
0.80	0.90	57.0	70.0	121.0	18.0	23.0	39.0	9.0	11.0	20.0
0.80	0.80	36.0	44.0	76.0	12.0	14.0	25.0	6.0	7.0	13.0
0.80	0.70	24.0	29.0	50.0	8.0	9.0	16.0	4.0	5.0	8.0

19 Lakes with 20 < ANC ≤ 100 μeq L^{-1}

		0.20 pH units			0.35 pH units			0.50 pH units		
1-α	1-β	Q_1	M	Q_4	Q_1	M	Q_4	Q_1	M	Q_4
0.95	0.95	181.0	249.0	489.0	59.0	81.0	158.0	30.0	41.0	81.0
0.95	0.90	144.0	198.0	388.0	46.0	64.0	125.0	24.0	33.0	64.0
0.95	0.80	104.0	143.0	280.0	34.0	46.0	91.0	17.0	24.0	46.0
0.95	0.70	79.0	109.0	213.0	26.0	35.0	69.0	13.0	18.0	35.0
0.90	0.95	144.0	198.0	388.0	46.0	64.0	125.0	24.0	33.0	64.0
0.90	0.90	111.0	152.0	299.0	36.0	49.0	97.0	18.0	25.0	49.0
0.90	0.80	76.0	105.0	205.0	25.0	34.0	66.0	13.0	17.0	34.0
0.90	0.70	55.0	76.0	149.0	18.0	24.0	48.0	9.0	12.0	25.0
0.80	0.95	104.0	143.0	280.0	34.0	46.0	91.0	17.0	24.0	46.0
0.80	0.90	76.0	105.0	205.0	25.0	34.0	66.0	13.0	17.0	34.0
0.80	0.80	48.0	66.0	130.0	16.0	21.0	42.0	8.0	11.0	21.0
0.80	0.70	32.0	44.0	85.0	10.0	14.0	28.0	5.0	7.0	14.0

TABLE E-6. REGIONAL DISTRIBUTIONS OF N, THE NUMBER OF SAMPLES REQUIRED TO DETECT THREE LEVELS OF CHANGE IN SO_4^{-2} IN VERMONT.

VERMONT
SO_4^{-2} μeq L^{-1}

11 Lakes with ANC < 20 μeq L^{-1}

		10%			25%			50%		
1-α	1-β	Q_1	M	Q_4	Q_1	M	Q_4	Q_1	M	Q_4
0.95	0.95	37.0	48.0	161.0	7.0	9.0	29.0	2.0	3.0	9.0
0.95	0.90	30.0	38.0	128.0	5.0	7.0	23.0	2.0	2.0	7.0
0.95	0.80	21.0	27.0	93.0	4.0	5.0	17.0	1.0	1.0	5.0
0.95	0.70	16.0	21.0	70.0	3.0	4.0	13.0	1.0	1.0	4.0
0.90	0.95	30.0	38.0	128.0	5.0	7.0	23.0	2.0	2.0	7.0
0.90	0.90	23.0	29.0	99.0	4.0	5.0	18.0	1.0	2.0	5.0
0.90	0.80	16.0	20.0	68.0	3.0	4.0	12.0	1.0	1.0	4.0
0.90	0.70	11.0	14.0	49.0	2.0	3.0	9.0	1.0	1.0	3.0
0.80	0.95	21.0	27.0	93.0	4.0	5.0	17.0	1.0	1.0	5.0
0.80	0.90	16.0	20.0	68.0	3.0	4.0	12.0	1.0	1.0	4.0
0.80	0.80	10.0	13.0	43.0	2.0	2.0	8.0	1.0	1.0	2.0
0.80	0.70	7.0	8.0	28.0	1.0	2.0	5.0	0.0	0.0	2.0

19 Lakes with 20 < ANC ≤ 100 μeq L^{-1}

		10%			25%			50%		
1-α	1-β	Q_1	M	Q_4	Q_1	M	Q_4	Q_1	M	Q_4
0.95	0.95	42.0	64.0	119.0	8.0	12.0	22.0	2.0	4.0	7.0
0.95	0.90	33.0	51.0	95.0	6.0	9.0	17.0	2.0	3.0	5.0
0.95	0.80	24.0	37.0	68.0	4.0	7.0	12.0	1.0	2.0	4.0
0.95	0.70	18.0	28.0	52.0	3.0	5.0	9.0	1.0	2.0	3.0
0.90	0.95	33.0	51.0	95.0	6.0	9.0	17.0	2.0	3.0	5.0
0.90	0.90	25.0	39.0	73.0	5.0	7.0	13.0	1.0	2.0	4.0
0.90	0.80	17.0	27.0	50.0	3.0	5.0	9.0	1.0	1.0	3.0
0.90	0.70	13.0	20.0	36.0	2.0	4.0	7.0	1.0	1.0	2.0
0.80	0.95	24.0	37.0	68.0	4.0	7.0	12.0	1.0	2.0	4.0
0.80	0.90	17.0	27.0	50.0	3.0	5.0	9.0	1.0	1.0	3.0
0.80	0.80	11.0	17.0	32.0	2.0	3.0	6.0	1.0	1.0	2.0
0.80	0.70	7.0	11.0	21.0	1.0	2.0	4.0	0.0	1.0	1.0

TABLE E-7. REGIONAL DISTRIBUTIONS OF N, THE NUMBER OF SAMPLES REQUIRED TO DETECT THREE LEVELS OF CHANGE IN ANC IN THE UPPER MIDWEST.

UPPER MIDWEST
ANC

13 Lakes with ANC < 20 μeq L^{-1}

		10 μeq L^{-1}			25 μeq L^{-1}			50 μeq L^{-1}		
1-α	1-β	Q_1	M	Q_4	Q_1	M	Q_4	Q_1	M	Q_4
0.95	0.95	17.0	23.0	37.0	3.0	4.0	7.0	1.0	1.0	2.0
0.95	0.90	13.0	18.0	29.0	2.0	3.0	5.0	1.0	1.0	2.0
0.95	0.80	9.0	13.0	21.0	2.0	2.0	4.0	1.0	1.0	1.0
0.95	0.70	7.0	10.0	16.0	1.0	2.0	3.0	0.0	1.0	1.0
0.90	0.95	13.0	18.0	29.0	2.0	3.0	5.0	1.0	1.0	2.0
0.90	0.90	10.0	14.0	23.0	2.0	3.0	4.0	1.0	1.0	1.0
0.90	0.80	7.0	10.0	16.0	1.0	2.0	3.0	0.0	1.0	1.0
0.90	0.70	5.0	7.0	11.0	1.0	1.0	2.0	0.0	0.0	1.0
0.80	0.95	9.0	13.0	21.0	2.0	2.0	4.0	1.0	1.0	1.0
0.80	0.90	7.0	10.0	16.0	1.0	2.0	3.0	0.0	1.0	1.0
0.80	0.80	4.0	6.0	10.0	1.0	1.0	2.0	0.0	0.0	1.0
0.80	0.70	3.0	4.0	6.0	1.0	1.0	1.0	0.0	0.0	0.0

8 Lakes with 20 < ANC ≤ 100 μeq L^{-1}

		10 μeq L^{-1}			25 μeq L^{-1}			50 μeq L^{-1}		
1-α	1-β	Q_1	M	Q_4	Q_1	M	Q_4	Q_1	M	Q_4
0.95	0.95	16.5	37.0	54.0	3.0	6.5	9.5	1.0	2.0	2.5
0.95	0.90	13.0	29.5	43.0	2.5	5.0	7.5	0.5	1.5	2.5
0.95	0.80	9.5	21.0	31.5	1.5	4.0	5.5	0.5	1.0	1.5
0.95	0.70	7.5	16.0	23.5	1.5	2.5	4.5	0.5	1.0	1.0
0.90	0.95	13.0	29.5	43.0	2.5	5.0	7.5	0.5	1.5	2.5
0.90	0.90	10.0	22.5	33.0	1.5	4.0	6.0	0.5	1.0	1.5
0.90	0.80	7.0	16.0	22.5	1.5	2.5	4.0	0.0	1.0	1.0
0.90	0.70	5.0	11.0	16.5	1.0	2.0	2.5	0.0	0.5	1.0
0.80	0.95	9.5	21.0	31.5	1.5	4.0	5.5	0.5	1.0	1.5
0.80	0.90	7.0	16.0	22.5	1.5	2.5	4.0	0.0	1.0	1.0
0.80	0.80	4.5	10.0	14.0	1.0	1.5	2.5	0.0	0.5	1.0
0.80	0.70	3.0	6.5	9.5	0.5	1.0	1.5	0.0	0.0	0.5

TABLE E-8. REGIONAL DISTRIBUTIONS OF N, THE NUMBER OF SAMPLES REQUIRED TO DETECT THREE LEVELS OF CHANGE IN pH IN THE UPPER MIDWEST.

UPPER MIDWEST
pH

13 Lakes with ANC < 20 μeq L^{-1}

		0.20 pH units			0.35 pH units			0.50 pH units		
1-α	1-β	Q_1	M	Q_4	Q_1	M	Q_4	Q_1	M	Q_4
0.95	0.95	6.0	13.0	20.0	2.0	4.0	6.0	1.0	2.0	3.0
0.95	0.90	5.0	11.0	16.0	2.0	3.0	5.0	1.0	2.0	3.0
0.95	0.80	3.0	8.0	11.0	1.0	2.0	4.0	1.0	1.0	2.0
0.95	0.70	3.0	6.0	9.0	1.0	2.0	3.0	0.0	1.0	1.0
0.90	0.95	5.0	11.0	16.0	2.0	3.0	5.0	1.0	2.0	3.0
0.90	0.90	4.0	8.0	12.0	1.0	3.0	4.0	1.0	1.0	2.0
0.90	0.80	2.0	6.0	8.0	1.0	2.0	3.0	0.0	1.0	1.0
0.90	0.70	2.0	4.0	6.0	1.0	1.0	2.0	0.0	1.0	1.0
0.80	0.95	3.0	8.0	11.0	1.0	2.0	4.0	1.0	1.0	2.0
0.80	0.90	2.0	6.0	8.0	1.0	2.0	3.0	0.0	1.0	1.0
0.80	0.80	2.0	4.0	5.0	1.0	1.0	2.0	0.0	1.0	1.0
0.80	0.70	1.0	2.0	3.0	0.0	1.0	1.0	0.0	0.0	1.0

8 Lakes with 20 < ANC ≤ 100 μeq L^{-1}

		0.20 pH units			0.35 pH units			0.50 pH units		
1-α	1-β	Q_1	M	Q_4	Q_1	M	Q_4	Q_1	M	Q_4
20.95	0.95	16.5	28.5	87.0	5.0	9.5	28.5	3.0	4.5	14.5
0.95	0.90	13.0	22.5	69.0	4.0	7.5	22.0	2.0	3.5	11.0
0.95	0.80	9.5	16.0	50.0	3.0	5.5	16.5	2.0	3.0	8.5
0.95	0.70	7.0	12.5	38.0	2.0	4.0	12.0	1.0	2.0	6.5
0.90	0.95	13.0	22.5	69.0	4.0	7.5	22.0	2.0	3.5	11.0
0.90	0.90	10.0	17.0	53.0	3.0	5.5	17.5	2.0	3.0	9.0
0.90	0.80	7.0	12.0	36.5	2.0	4.0	12.0	1.0	2.0	6.0
0.90	0.70	5.0	8.5	26.5	2.0	3.0	8.5	1.0	1.0	4.5
0.80	0.95	9.5	16.0	50.0	3.9	5.5	16.5	2.0	3.0	8.5
0.80	0.90	7.0	12.0	36.5	2.0	4.0	12.0	1.0	2.0	6.0
0.80	0.80	4.0	7.5	23.0	1.0	2.5	7.5	1.0	1.0	3.5
0.80	0.70	3.0	5.0	15.5	1.0	2.0	4.5	0.0	1.0	2.5

TABLE E-9. REGIONAL DISTRIBUTIONS OF N, THE NUMBER OF SAMPLES REQUIRED TO DETECT THREE LEVELS OF CHANGE IN SO_4^{-2} IN THE UPPER MIDWEST.

UPPER MIDWEST
SO_4^{-2} μeq L^{-1}

13 Lakes with ANC < 20 μeq L^{-1}

		10%			25%			50%		
1-α	1-β	Q_1	M	Q_4	Q_1	M	Q_4	Q_1	M	Q_4
0.95	0.95	10.0	13.0	28.0	2.0	2.0	5.0	1.0	1.0	2.0
0.95	0.90	8.0	10.0	22.0	1.0	2.0	4.0	0.0	1.0	1.0
0.95	0.80	6.0	7.0	16.0	1.0	1.0	3.0	0.0	0.0	1.0
0.95	0.70	4.0	6.0	12.0	1.0	1.0	2.0	0.0	0.0	1.0
0.90	0.95	8.0	10.0	22.0	1.0	2.0	4.0	0.0	1.0	1.0
0.90	0.90	6.0	8.0	17.0	1.0	1.0	3.0	0.0	0.0	1.0
0.90	0.80	4.0	5.0	12.0	1.0	1.0	2.0	0.0	0.0	1.0
0.90	0.70	3.0	4.0	8.0	1.0	1.0	2.0	0.0	0.0	0.0
0.80	0.95	6.0	7.0	16.0	1.0	1.0	3.0	0.0	0.0	1.0
0.80	0.90	4.0	5.0	12.0	1.0	1.0	2.0	0.0	0.0	1.0
0.80	0.80	3.0	3.0	7.0	0.0	1.0	1.0	0.0	0.0	0.0
0.80	0.70	2.0	2.0	5.0	0.0	0.0	1.0	0.0	0.0	0.0

8 Lakes with 20 < ANC ≤ 100 μeq L^{-1}

		10%			25%			50%		
1-α	1-β	Q_1	M	Q_4	Q_1	M	Q_4	Q_1	M	Q_4
0.95	0.95	22.5	43.0	216.5	4.0	7.5	39.5	1.5	2.5	11.5
0.95	0.90	17.5	34.0	172.0	3.0	6.0	31.0	1.0	1.5	9.5
0.95	0.80	13.0	25.0	124.5	2.5	4.5	22.5	0.5	1.5	7.0
0.95	0.70	10.0	19.0	95.0	1.5	3.5	17.5	0.5	1.0	5.0
0.90	0.95	17.5	34.0	172.0	3.0	6.0	31.0	1.0	1.5	9.5
0.90	0.90	14.0	26.5	133.0	2.5	5.0	24.0	1.0	1.5	7.0
0.90	0.80	9.5	18.0	91.0	1.5	3.5	16.5	0.5	1.0	5.0
0.90	0.70	7.0	13.0	66.0	1.5	2.5	12.0	0.0	1.0	4.0
0.80	0.95	13.0	25.0	124.5	2.5	4.5	22.5	0.5	1.5	7.0
0.80	0.90	9.5	18.0	91.0	1.5	3.5	16.5	0.5	1.0	5.0
0.80	0.80	6.0	11.5	57.5	1.0	2.5	10.5	0.0	0.5	3.0
0.80	0.70	4.0	7.5	38.0	0.5	1.5	7.0	0.0	0.0	2.0

TABLE E-10. REGIONAL DISTRIBUTIONS OF N, THE NUMBER OF SAMPLES REQUIRED TO DETECT THREE LEVELS OF CHANGE IN ANC IN MICHIGAN.

MICHIGAN
ANC

6 Lakes with ANC < 20 μeq L^{-1}

		10 μeq L^{-1}			25 μeq L^{-1}			50 μeq L^{-1}		
1-α	1-β	Q_1	M	Q_4	Q_1	M	Q_4	Q_1	M	Q_4
0.95	0.95	17.0	30.0	41.0	3.0	5.5	8.0	1.0	1.5	3.0
0.95	0.90	13.0	23.5	33.0	2.0	4.0	6.0	1.0	1.5	2.0
0.95	0.80	9.0	17.0	24.0	2.0	3.0	5.0	1.0	1.0	2.0
0.95	0.70	7.0	13.0	18.0	1.0	2.5	4.0	0.0	1.0	1.0
0.90	0.95	13.0	23.5	33.0	2.0	4.0	6.0	1.0	1.5	2.0
0.90	0.90	10.0	18.5	25.0	2.0	3.5	5.0	1.0	1.0	2.0
0.90	0.80	7.0	13.0	17.0	1.0	2.5	3.0	0.0	1.0	1.0
0.90	0.70	5.0	9.0	13.0	1.0	1.5	2.0	0.0	0.5	1.0
0.80	0.95	9.0	17.0	24.0	2.0	3.0	5.0	1.0	1.0	2.0
0.80	0.90	7.0	13.0	17.0	1.0	2.5	3.0	0.0	1.0	1.0
0.80	0.80	4.0	8.0	11.0	1.0	1.5	2.0	0.0	0.5	1.0
0.80	0.70	3.0	5.0	7.0	1.0	1.0	1.0	0.0	0.0	0.0

TABLE E-11. REGIONAL DISTRIBUTIONS OF N, THE NUMBER OF SAMPLES REQUIRED TO DETECT THREE LEVELS OF CHANGE IN pH IN MICHIGAN.

MICHIGAN
pH

6 Lakes with ANC < 20 μeq L^{-1}

		0.20 pH units			0.35 pH units			0.50 pH units		
1-α	1-β	Q_1	M	Q_4	Q_1	M	Q_4	Q_1	M	Q_4
0.95	0.95	4.0	8.5	13.0	1.0	3.0	4.0	1.0	1.5	2.0
0.95	0.90	3.0	7.0	10.0	1.0	2.0	3.0	1.0	1.5	2.0
0.95	0.80	2.0	5.0	7.0	1.0	1.5	2.0	0.0	1.0	1.0
0.95	0.70	2.0	3.5	6.0	1.0	1.5	2.0	0.0	0.5	1.0
0.90	0.95	3.0	7.0	10.0	1.0	2.0	3.0	1.0	1.5	2.0
0.90	0.90	3.0	5.0	8.0	1.0	1.5	3.0	0.0	1.0	1.0
0.90	0.80	2.0	3.5	5.0	1.0	1.5	2.0	0.0	0.5	1.0
0.90	0.70	1.0	3.0	4.0	0.0	1.0	1.0	0.0	0.5	1.0
0.80	0.95	2.0	5.0	7.0	1.0	1.5	2.0	0.0	1.0	1.0
0.80	0.90	2.0	3.5	5.0	1.0	1.5	2.0	0.0	0.5	1.0
0.80	0.80	1.0	2.0	3.0	0.0	0.5	1.0	0.0	0.5	1.0
0.80	0.70	1.0	1.5	2.0	0.0	0.5	1.0	0.0	0.0	0.0

TABLE E-12. REGIONAL DISTRIBUTIONS OF N, THE NUMBER OF SAMPLES REQUIRED TO DETECT THREE LEVELS OF CHANGE IN SO_4^{-2} IN MICHIGAN.

MICHIGAN
SO_4^{-2} μeq L^{-1}

6 Lakes with ANC < 20 μeq L^{-1}

		10%			25%			50%		
1-α	1-β	Q_1	M	Q_4	Q_1	M	Q_4	Q_1	M	Q_4
0.95	0.95	6.0	10.0	18.0	1.0	2.0	3.0	0.0	0.5	1.0
0.95	0.90	5.0	8.5	14.0	1.0	1.5	3.0	0.0	0.5	1.0
0.95	0.80	4.0	6.0	10.0	1.0	1.0	2.0	0.0	0.0	1.0
0.95	0.70	3.0	4.5	8.0	1.0	1.0	1.0	0.0	0.0	0.0
0.90	0.95	5.0	8.5	14.0	1.0	1.5	3.0	0.0	0.5	1.0
0.90	0.90	4.0	6.5	11.0	1.0	1.0	2.0	0.0	0.0	1.0
0.90	0.80	3.0	4.5	7.0	0.0	1.0	1.0	0.0	0.0	0.0
0.90	0.70	2.0	3.5	5.0	0.0	0.5	1.0	0.0	0.0	0.0
0.80	0.95	4.0	6.0	10.0	1.0	1.0	2.0	0.0	0.0	1.0
0.80	0.90	3.0	4.5	7.0	0.0	1.0	1.0	0.0	0.0	0.0
0.80	0.80	2.0	2.5	5.0	0.0	0.5	1.0	0.0	0.0	0.0
0.80	0.70	1.0	1.5	3.0	0.0	0.0	1.0	0.0	0.0	0.0

TABLE E-13. REGIONAL DISTRIBUTIONS OF N, THE NUMBER OF SAMPLES REQUIRED TO DETECT THREE LEVELS OF CHANGE IN ANC IN WISCONSIN.

WISCONSIN
ANC

6 Lakes with ANC < 20 μeq L^{-1}

		10 μeq L^{-1}			25 μeq L^{-1}			50 μeq L^{-1}		
1-α	1-β	Q_1	M	Q_4	Q_1	M	Q_4	Q_1	M	Q_4
0.95	0.95	13.0	19.0	29.0	2.0	3.5	5.0	1.0	1.0	2.0
0.95	0.90	10.0	15.0	23.0	2.0	3.0	4.0	1.0	1.0	1.0
0.95	0.80	7.0	11.0	17.0	1.0	2.0	3.0	0.0	1.0	1.0
0.95	0.70	6.0	8.5	13.0	1.0	1.5	2.0	0.0	0.0	1.0
0.90	0.95	10.0	15.0	23.0	2.0	3.0	4.0	1.0	1.0	1.0
0.90	0.90	8.0	11.5	18.0	1.0	2.0	3.0	0.0	1.0	1.0
0.90	0.80	5.0	8.0	12.0	1.0	1.5	2.0	0.0	0.0	1.0
0.90	0.70	4.0	5.5	9.0	1.0	1.0	2.0	0.0	0.0	0.0
0.80	0.95	7.0	11.0	17.0	1.0	2.0	3.0	0.0	1.0	1.0
0.80	0.90	5.0	8.0	12.0	1.0	1.5	2.0	0.0	0.0	1.0
0.80	0.80	3.0	5.0	8.0	1.0	1.0	1.0	0.0	0.0	0.0
0.80	0.70	2.0	3.5	5.0	0.0	1.0	1.0	0.0	0.0	0.0

5 Lakes with 20 < ANC ≤ 100 μeq L^{-1}

		10 μeq L^{-1}			25 μeq L^{-1}			50 μeq L^{-1}		
1-α	1-β	Q_1	M	Q_4	Q_1	M	Q_4	Q_1	M	Q_4
0.95	0.95	11.0	30.0	44.0	2.0	5.0	8.0	1.0	2.0	2.0
0.95	0.90	9.0	24.0	35.0	2.0	4.0	6.0	0.0	1.0	2.0
0.95	0.80	6.0	17.0	25.0	1.0	3.0	5.0	0.0	1.0	1.0
0.95	0.70	5.0	13.0	19.0	1.0	2.0	3.0	0.0	1.0	1.0
0.90	0.95	9.0	24.0	35.0	2.0	4.0	6.0	0.0	1.0	2.0
0.90	0.90	7.0	18.0	27.0	1.0	3.0	5.0	0.0	1.0	1.0
0.90	0.80	5.0	13.0	19.0	1.0	2.0	3.0	0.0	1.0	1.0
0.90	0.70	3.0	9.0	13.0	1.0	2.0	2.0	0.0	0.0	1.0
0.80	0.95	6.0	17.0	25.0	1.0	3.0	5.0	0.0	1.0	1.0
0.80	0.90	5.0	13.0	19.0	1.0	2.0	3.0	0.0	1.0	1.0
0.80	0.80	3.0	8.0	12.0	1.0	1.0	2.0	0.0	0.0	1.0
0.80	0.70	2.0	5.0	8.0	0.0	1.0	1.0	0.0	0.0	0.0

TABLE E-14. REGIONAL DISTRIBUTIONS OF N, THE NUMBER OF SAMPLES REQUIRED TO DETECT THREE LEVELS OF CHANGE IN pH IN WISCONSIN.

WISCONSIN
pH

6 Lakes with ANC < 20 μeq L^{-1}

		0.20 pH units			0.35 pH units			0.50 pH units		
1-α	1-β	Q_1	M	Q_4	Q_1	M	Q_4	Q_1	M	Q_4
0.95	0.95	19.0	22.0	24.0	6.0	7.0	8.0	3.0	3.5	4.0
0.95	0.90	15.0	17.5	19.0	5.0	5.5	6.0	3.0	3.0	3.0
0.95	0.80	11.0	12.5	14.0	4.0	4.0	5.0	2.0	2.0	2.0
0.95	0.70	8.0	10.0	11.0	3.0	3.0	3.0	1.0	1.5	2.0
0.90	0.95	15.0	17.5	19.0	5.0	5.5	6.0	3.0	3.0	3.0
0.90	0.90	12.0	13.5	15.0	4.0	4.5	5.0	2.0	2.0	2.0
0.90	0.80	8.0	9.0	10.0	3.0	3.0	3.0	1.0	1.5	2.0
0.90	0.70	6.0	6.5	7.0	2.0	2.0	2.0	1.0	1.0	1.0
0.80	0.95	11.0	12.5	14.0	4.0	4.0	5.0	2.0	2.0	2.0
0.80	0.90	8.0	9.0	10.0	3.0	3.0	3.0	1.0	1.5	2.0
0.80	0.80	5.0	5.5	6.0	2.0	2.0	2.0	1.0	1.0	1.0
0.80	0.70	3.0	3.5	4.0	1.0	1.0	1.0	1.0	1.0	1.0

5 Lakes with 20 < ANC ≤ 100 μeq L^{-1}

		0.20 pH units			0.35 pH units			0.50 pH units		
1-α	1-β	Q_1	M	Q_4	Q_1	M	Q_4	Q_1	M	Q_4
0.95	0.95	17.0	27.0	79.0	5.0	9.0	26.0	3.0	4.0	13.0
0.95	0.90	13.0	21.0	63.0	4.0	7.0	20.0	2.0	3.0	10.0
0.95	0.80	10.0	15.0	46.0	3.0	5.0	15.0	2.0	3.0	8.0
0.95	0.70	7.0	12.0	35.0	2.0	4.0	11.0	1.0	2.0	6.0
0.90	0.95	13.0	21.0	63.0	4.0	7.0	20.0	2.0	3.0	10.0
0.90	0.90	10.0	16.0	48.0	3.0	5.0	16.0	2.0	3.0	8.0
0.90	0.80	7.0	11.0	33.0	2.0	4.0	11.0	1.0	2.0	5.0
0.90	0.70	5.0	8.0	24.0	2.0	3.0	8.0	1.0	1.0	4.0
0.80	0.95	10.0	15.0	46.0	3.0	5.0	15.0	2.0	3.0	8.0
0.80	0.90	7.0	11.0	33.0	2.0	4.0	11.0	1.0	2.0	5.0
0.80	0.80	4.0	7.0	21.0	1.0	2.0	7.0	1.0	1.0	3.0
0.80	0.70	3.0	5.0	14.0	1.0	2.0	4.0	0.0	1.0	2.0

TABLE E-15. REGIONAL DISTRIBUTIONS OF N, THE NUMBER OF SAMPLES REQUIRED TO DETECT THREE LEVELS OF CHANGE IN SO_4^{-2} IN WISCONSIN.

WISCONSIN
SO_4^{-2} $\mu eq\ L^{-1}$

6 Lakes with ANC < 20 $\mu eq\ L^{-1}$

		10%			25%			50%		
1-α	1-β	Q_1	M	Q_4	Q_1	M	Q_4	Q_1	M	Q_4
0.95	0.95	13.0	22.0	29.0	2.0	4.0	5.0	1.0	1.5	2.0
0.95	0.90	10.0	17.5	23.0	2.0	3.0	4.0	1.0	1.0	1.0
0.95	0.80	7.0	12.5	16.0	1.0	2.5	3.0	0.0	1.0	1.0
0.95	0.70	6.0	9.5	13.0	1.0	1.5	2.0	0.0	0.5	1.0
0.90	0.95	10.0	17.5	23.0	2.0	3.0	4.0	1.0	1.0	1.0
0.90	0.90	8.0	13.5	18.0	1.0	2.5	3.0	0.0	1.0	1.0
0.90	0.80	5.0	9.5	12.0	1.0	1.5	2.0	0.0	0.5	1.0
0.90	0.70	4.0	6.5	9.0	1.0	1.5	2.0	0.0	0.0	0.0
0.80	0.95	7.0	12.5	16.0	1.0	2.5	3.0	0.0	1.0	1.0
0.80	0.90	5.0	9.5	12.0	1.0	1.5	2.0	0.0	0.5	1.0
0.80	0.80	3.0	5.5	8.0	1.0	1.0	1.0	0.0	0.0	0.0
0.80	0.70	2.0	4.0	5.0	0.0	1.0	1.0	0.0	0.0	0.0

5 Lakes with 20 < ANC ≤ 100 $\mu eq\ L^{-1}$

		10%			25%			50%		
1-α	1-β	Q_1	M	Q_4	Q_1	M	Q_4	Q_1	M	Q_4
0.95	0.95	34.0	52.0	97.0	6.0	9.0	18.0	2.0	3.0	5.0
0.95	0.90	27.0	41.0	77.0	5.0	7.0	14.0	1.0	2.0	4.0
0.95	0.80	20.0	30.0	56.0	4.0	5.0	10.0	1.0	2.0	3.0
0.95	0.70	15.0	23.0	43.0	3.0	4.0	8.0	1.0	1.0	2.0
0.90	0.95	27.0	41.0	77.0	5.0	7.0	14.0	1.0	2.0	4.0
0.90	0.90	21.0	32.0	60.0	4.0	6.0	11.0	1.0	2.0	3.0
0.90	0.80	14.0	22.0	41.0	3.0	4.0	7.0	1.0	1.0	2.0
0.90	0.70	10.0	16.0	30.0	2.0	3.0	5.0	1.0	1.0	2.0
0.80	0.95	20.0	30.0	56.0	4.0	5.0	10.0	1.0	2.0	3.0
0.80	0.90	14.0	22.0	41.0	3.0	4.0	7.0	1.0	1.0	2.0
0.80	0.80	9.0	14.0	26.0	2.0	3.0	5.0	0.0	1.0	1.0
0.80	0.70	6.0	9.0	17.0	1.0	2.0	3.0	0.0	0.0	1.0

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